Kinetic Theory and Stochastic Processes

I. OVERVIEW

Kinetic theory stems from early attempts to derive macroscopic laws governing the behavior of large systems starting with the laws governing the interaction of microscopic constituents. In general the kinetic theory deals with the interrelation of the laws operating at different levels of description of the same system. Normally one level is more fundamental and it provides a more detailed description of the system, while the other gives a reduced description of the system. An example is provided by the equilibrium statistical mechanics where instead of describing a macroscopic system by about 10^{23} dynamical variables characterizing atomic positions and velocities one uses just a few macroscopic variables. It is essential that the relations between the macroscopic variables are closed. These variables and the relations between them constitute but one example of the so-called collective variables and reduced description.

Nature is full of sometimes surprising mathematical relations at all levels. For example, a recent study has shown that that the citation distribution, that is the numbers of papers $N(x)$ that has been cited a total of x times, - has a power-law tail, $N(x) \sim x^{-\alpha}$ with $\alpha \approx 3$. Now suppose you would set the task of explaining why this law is observed. It would not be very wise to start with the molecular dynamics and to try to derive the law from the first principles. Yet this does not mean that the task itself is not feasible. In order to describe the observed behavior, one would try to introduce certain collective variables that would describe the behavior of either single humans or whole groups of humans and would try to write their effective or reduced dynamics that would be approximately closed. In other words, one would try to construct a reduced description of the system. In fact, one could expect that a certain mathematical behavior would govern the tail of $N(x)$ just because it is formed by collective effects: minimally cited papers are usually referenced by their authors and their close associates, while heavily cited papers become known through collective effects.

A general question addressed by the kinetic theory is: knowing the laws at one level of description, are there new, collective laws that appear at a higher level? And if yes, how can one derive them? These tantalizing questions pass through the whole of physics. The new laws are sometimes called "emergent", while the laws at a lower level "fundamental" or "first principles". It should be emphasized that more often than not, we cannot derive the emergent laws from the first principles. In the "derivation" there is almost always a tacit assumption that should be taken for granted. However, often one can get sufficiently close to the actual derivation of the emergent laws in order to determine their form.

A very important notion for deriving the laws at higher level from the laws of the lower level is time scale separation. Time scale separation holds when the system can be characterized by two sets of variables with vastly different dynamical time-scales. To identify the sets one looks for the variables with large time-scale of the dynamics, i. e. *slow variables*. For example, such variables could be provided by "almost" integrals of motion that is variables that become integrals of motion when a certain limit in the parameters of the system is taken. Once the separation into slow and fast variables is done, one eliminates the time-scales associated with the fast dynamics to derive an approximate closed dynamics for the slow variables(*reduced dynamics*). Still the dynamics is closed only approximately and it has corrections due to the impact of the discarded fast variables. It turns out that often the remaining effect of the fast variables can be described by adding some noise to the equations which turns the dynamics of the slow variables into a stochastic equation.

An important property that emerges often when passing to the reduced dynamics is irreversibility. Suppose that at some initial moment of time, we know the value of the variables of the reduced dynamics but we have discarded the values of the rest of the variables of the system. As the system evolves, our uncertainty about the value of the variables of the reduced dynamics, which was initially equal to zero, grows. This is because different initial values of the discarded variables become consistent with more and more values of the variables of the reduced dynamics. Such loss of information is described by the increase in entropy. Here we rely on the interpretation of the entropy as a measure of the missing information on the system that comes from the information theory providing an alternative outlook on the statistical physics in equilibrium. On the formal level, the growth of the entropy is caused by the noise terms in the equations.

Let us illustrate some of the notions above by a simple example.

II. THE SIMPLEST CASE OF TIME SEPARATION AND EMERGENT DYNAMICS: WEAKLY PERTURBED HARMONIC OSCILLATOR

A simplest example of time separation is provided by the harmonic oscillator perturbed by weak linear damping. In rescaled variables the oscillator equation is given by

$$\ddot{x} + \epsilon \dot{x} + x = 0, \tag{1}$$

where $x(t)$ is the coordinate. The exact solution is well-known

$$x(t) = A e^{-\epsilon t/2} \cos\left[\sqrt{1 - \frac{\epsilon^2}{4}} t + \Phi\right], \tag{2}$$

where A and Φ are constants. We see that at $\epsilon \ll 1$ there appear two vastly separated time-scales in the dynamics: the natural frequency time-scale of order one and the damping time-scale $1/\epsilon$. At a time-scale of order one the motion of the oscillator is very close to the motion of the undamped oscillator. If we make the local harmonic oscillator substitution

$$x(t) = a(t) \cos\left[t + \phi(t)\right], \tag{3}$$

then at a time-scale of order one, both $a(t) = A\exp[-\epsilon t/2]$ and $\phi(t) \approx \Phi - \epsilon^2 t/2$ are "almost constant". We may refer to $a(t)$ and $\phi(t)$ as *slow variables*. Now let us assume we were only interested in the gross dynamics occurring at a time-scale much larger than one. At this time-scale the main qualitative feature of the dynamics is the decay of the energy of the unperturbed oscillator $E(t) \equiv \dot{x}^2/2 + x^2/2$. Substituting into $E(t)$ the expression (2) for $x(t)$ we have

$$E(t) = \frac{A^2 e^{-\epsilon t}}{2} + \frac{A^2 \epsilon^2 e^{-\epsilon t} \cos^2\left[\sqrt{1 - \frac{\epsilon^2}{4}} t + \Phi\right]}{8} + \frac{A^2 \left[\sqrt{1 - \epsilon^2/4} - 1\right] e^{-\epsilon t} \sin^2\left[\sqrt{1 - \frac{\epsilon^2}{4}} t + \Phi\right]}{8}. \tag{4}$$

If we are not interested in the small fast wiggles around the main term, we obtain just $E(t) \approx A^2 \exp[-t]/2$. Let us show now that we could obtain this simple result without employing the exact solution. We note that the exact equation of the energy decay is $\dot{E} = -\epsilon \dot{x}^2$, where $\dot{x}^2$ term changes at the time-scale of order one. However, due to the prefactor ϵ, the energy varies at the time-scale $1/\epsilon$. To use the separation of time-scales we introduce the operation of *partial time-averaging*

$$\langle E \rangle_{\Delta t}(t) \equiv \int_t^{t+\Delta t} \frac{dt'}{\Delta t} E(t'), \tag{5}$$

where Δt is a separation time-scale satisfying $1 \ll \Delta t \ll 1/\epsilon$. Note that partial time-averaging commutes with derivative:

$$\frac{d}{dt}\langle g \rangle_{\Delta t}(t) = \frac{d}{dt}\int_t^{t+\Delta t} \frac{dt'}{\Delta t} g(t') = \frac{g(t+\Delta t) - g(t)}{\Delta t} = \int_t^{t+\Delta t} \frac{dt'}{\Delta t}\frac{dg}{dt'} \tag{6}$$

where $g(t)$ is an arbitrary function of time. Due to $\Delta t \ll 1/\epsilon$ we have $E(t) \approx \langle E \rangle_{\Delta t}(t)$, and we can write

$$\frac{dE}{dt} \approx \frac{d}{dt}\langle E \rangle_{\Delta t} = \int_t^{t+\Delta t} \frac{dt'}{\Delta t}\frac{dE}{dt'} = -\epsilon \int_t^{t+\Delta} \frac{dt'}{\Delta t}\dot{x}^2. \tag{7}$$

Next we note that at the time-scale $\Delta t \ll 1/\epsilon$, the coordinate $x(t)$ behaves as harmonic oscillator with energy which is approximately $E(t)$ and the period of oscillations close to one. As a result we have $\int_t^{t+\Delta t} \dot{x}^2 dt'/\Delta t \approx E(t)$ and the above equation reproduces the approximate exponential decay law of the energy.

While in the above simple example the use of the averaging method is of course not necessary, the method becomes a powerful tool of analysis of the general problem of perturbed harmonic oscillator

$$\frac{d^2 x}{dt^2} + x = \epsilon f\left(x, \frac{dx}{dt}\right), \tag{8}$$

where f is some function characterizing the perturbation. The general approach is as follows. The above system is equivalent to a system of ODE in the phase space with two degrees of freedom

$$\dot{x} = y, \quad \dot{y} = -x + \epsilon f(x, y), \tag{9}$$

where $y = \dot{x}$. To treat this system we note that at small ϵ, at time-scale of order one, the motion is very close to the motion of harmonic oscillator. To use this we make the local harmonic oscillator substitution of variables $x = a\cos\theta$ and $y = -a\sin\theta$ (at $\epsilon = 0$ we have $a = const$ and $\theta = t + const$). The substitution separates variables of the system into slow ones (the amplitude) and fast ones (the phase). The substitution can be viewed as the introduction of polar coordinates in the phase plane of the system and it is equivalent to the method of variation of parameters. We have

$$\dot{a}\cos\theta - a\dot{\theta}\sin\theta = -a\sin\theta, \quad -\dot{a}\sin\theta - a\dot{\theta}\cos\theta = -a\cos\theta + \epsilon f(a\cos\theta, -a\sin\theta), \tag{10}$$

or

$$\dot{a} = -\epsilon\sin\theta f(a\cos\theta, -a\sin\theta), \quad \dot{\theta} = 1 - \frac{\epsilon\cos\theta f(a\cos\theta, -a\sin\theta)}{a}. \tag{11}$$

To use the separation of time-scales of a and θ, we note that the equation on the amplitude is similar to the equation on the energy $E(t)$ above: the time derivative is proportional to the small parameter times some function including fast oscillating factors $\cos\theta$ and $\sin\theta$. Again we eliminate fast dynamics taking place at time-scale of order one by partial time averaging of the above equations over a time-scale Δt obeying $1 \ll \Delta t \ll 1/\epsilon$. Performing partial time-averaging of Eqs. (11) and using $\dot{a} \approx \langle\dot{a}\rangle_{\Delta t}$ and $\dot{\theta} \approx \langle\dot{\theta}\rangle_{\Delta t}$, where the last equality follows from the slowness of $\theta - t$ rather than θ itself, we obtain the approximate dynamics

$$\frac{da}{dt} = F[a(t)], \quad \frac{d\theta}{dt} = \omega[a(t)], \tag{12}$$

where

$$F \equiv -\epsilon\int_t^{t+\Delta}\frac{dt'}{\Delta t}\sin\theta(t')f[a(t')\cos\theta(t'), -a(t')\sin\theta(t')] \approx -\epsilon\int_0^{2\pi}\frac{d\phi}{2\pi}\sin\phi f[a(t)\cos\phi, -a(t)\sin\phi], \tag{13}$$

and the effective frequency of oscillations ω is

$$\omega \approx 1 - \frac{\epsilon}{a(t)}\int_0^{2\pi}\frac{d\phi}{2\pi}\cos t' f[a(t)\cos\phi, -a(t)\sin\phi]. \tag{14}$$

The inequality $1 \ll \Delta t \ll 1/\epsilon$ is crucial for the above manipulations - $\Delta t \ll 1/\epsilon$ allows to consider $a(t)$ as constant during the time interval of the integration, while $1 \ll \Delta t$ allows us not to care about the modulation of the phase $\theta(t) \approx t$ in the integrand and it allows to substitute the time average by the average over the period. The resulting evolution of a and θ provides an approximation to the true evolution similar to approximating $E(t)$ in Eq. (4) by the first term. To give an example of the use of the above procedure, consider the so-called Van der Pol oscillator

$$\frac{d^2x}{dt^2} + x = \epsilon(1 - x^2)\frac{dx}{dt}, \tag{15}$$

that corresponds to $f(x, y) = (1 - x^2)y$ in Eq. (8). The above equation first appeared in engineering and later was found useful as an example of deterministic chaos. At small damping, $\epsilon \ll 1$ we may use the averaging method for the study of the oscillator motion. We find

$$F = \epsilon a\int_0^{2\pi}\frac{d\phi}{2\pi}\sin^2\phi\left[1 - a^2\cos^2\phi\right] = \frac{\epsilon}{8}a(4 - a^2), \quad w = 1 + \epsilon\int_0^{2\pi}\frac{d\phi}{2\pi}\cos\phi\sin\phi\left[1 - a^2\cos^2\phi\right] = 1. \tag{16}$$

We conclude that at a time-scale long compared with the time-scale of fast oscillations, in the leading order in ϵ, the dynamics of Van der Pol oscillator takes the form

$$\frac{da}{dt} = \frac{\epsilon}{8}a(4 - a^2), \quad \frac{d\theta}{dt} = 1. \tag{17}$$

Thus the motion of the system consists of oscillations with the natural frequency and slowly modulated amplitude changing according to the first of the equations above. We observe that the amplitude evolves until it stabilizes at $a = 2$ where the system has a limit cycle.

The dynamics described by Eq. (17) is not of of the general form (12) - for Van der Pol oscillator the correction to the frequency vanishes in the leading order in ϵ and appears only in higher orders. You are invited to consider a different situation in the problem set.

To check that the reduced dynamics (12) is reasonable let us consider the case where the perturbation is such that the system remains Hamiltonian. This is the situation where $f(x, dx/dt)$ in Eq. (8) is function of x only, $f(x, dx/dt) = \tilde{f}(x)$. In this case we have

$$F = -\epsilon \int_0^{2\pi} \frac{d\phi}{2\pi} \tilde{f}[a(t)\cos\phi] \sin\phi = 0, \tag{18}$$

where the last identity is easily seen with the help of change of variables $\phi = 2\pi - \alpha$:

$$\int_0^{2\pi} \frac{d\phi}{2\pi} \tilde{f}[a(t)\cos\phi] \sin\phi = \int_0^{2\pi} \frac{d\alpha}{2\pi} \tilde{f}[a(t)\cos(2\pi-\alpha)] \sin(2\pi-\alpha) = -\int_0^{2\pi} \frac{d\alpha}{2\pi} \tilde{f}[a(t)\cos\alpha] \sin\alpha. \tag{19}$$

Thus the reduced dynamics (12) produces constant amplitude $\dot{a} = 0$ in the case of Hamiltonian systems. This is just what we should get on general grounds: we deal with a one-dimensional mechanical system where the form of the potential imposes a finite periodic motion with constant amplitude. The motion is however not purely sinusoidal and the amplitude is a non-trivial function of ϵ and initial conditions.

Let us now learn the main lesson of this section. We have started with dynamics in two dimensional phase space which is described by Eqs. (9). Then we passed to different variables in the phase space. These variables have the special property of time separation: the time-scale τ_s of variations of one variable (slow variable) is much larger than the time-scale τ_f of variations of the other (fast variable), $\tau_s \gg \tau_f$. We eliminated the dynamics at the time-scale of the fast variable by averaging over a separation time-scale Δt satisfying $\tau_f \ll \Delta t \ll \tau_s$. Thanks to the separation of time-scales, the obtained dynamics is again *local in time*. Moreover, the dynamics of the slow variable is closed, $\dot{a} = F(a)$, while the dynamics of the fast variable is driven by the slow variable, $\dot{\theta} = \omega(a)$. One says that the fast variable is *enslaved* by the slow one. Thus we passed from the original, local in time dynamics, to the reduced or emergent dynamics that takes place at a long time-scale but it is again local in time. This new dynamics admits simple interpretation in our case. Let us consider how the position of the phase space point $(x(t), y(t))$ changes according to Eqs. (9). After the time interval equal to the period 2π of the unperturbed oscillator the phase space point almost returns to the same position but both its amplitude a and its phase θ (the latter considered modulo 2π) possess certain increments due to small but finite ϵ. After another period 2π, the variables acquire additional small increments and so further. The expression for these increments constitutes the basis for a new dynamics that due to the increments smallness again has the form of ODE local in time. This is the reason why the reduced dynamics (12) is determined by integrals (13) and (14) over the period 2π. The emergent dynamics is a significant reduction in the complexity of the problem.

The above paradigm of separating the phase space variables into fast and slow ones and writing an effective closed dynamics for the slow variables is very important for the understanding of the equations appearing in the kinetic theory. Moreover, the paradigm is important for the understanding of the general question in physics: how comes that we can describe certain domain of situations without knowing the fundamental laws of nature to the end? The answer is that at every level new effective laws can be formulated where all physics at the more fundamental level is absorbed in some constants or functions (this is in accord with the ideas of renormalization group). In the case considered in this section, the dynamics at the "fundamental" level is determined by a function of two variables $f(x, y)$ appearing in Eqs. (9) while the dynamics at the next level of complexity is determined by two functions of one variable, $F(a)$ and $\omega(a)$, appearing in Eq. (9). In passage from one level to another, loss of information occurs - *different* $f(x, y)$ may result in the *same* $F(a)$ and $\omega(a)$, so that observations of the dynamics at long time-scale would give us no access to the fundamental dynamics of the system.

III. THERMODYNAMICS AND TIME SEPARATION

Time separation is also essential for understand the equations governing ordinary thermodynamic processes. Some of those equations can be actually derived if one knows how to perform the partial time averaging the molecular time-scales associated with molecular motion. There exists an important class of systems where such averaging can be performed explicitly. These are the so-called ergodic systems. Below we consider some thermodynamic processes and show how the relations describing them arise from the ergodicity assumption.

Recall that thermodynamics distinguishes two kinds of processes: reversible and irreversible ones. A reversible process is quasi-static so that the system always remains infinitesimally close to the thermodynamic equilibrium. For each step of a reversible process, the state variables have a well-defined meaning. How do we decide which process is quasi-static and which not? It is clear that the process must be slow, but how slow?

Before we address the above question, let us illustrate it using the example of an adiabatic thermodynamic process. During such a process the system is insulated and its dynamics is determined by a Hamiltonian $H[\boldsymbol{p}, \boldsymbol{q}, \lambda(t)]$ (here

and below $\boldsymbol{p}$ and $\boldsymbol{q}$ will stand for all momenta and coordinates of the system). The change of the equilibrium state of the system is caused by the change of the external parameter $\lambda(t)$. A most familiar example of the parameter λ is the volume V of the system, when the process takes place due to a change of the system volume at thermally insulated walls (note that in Hamiltonian formalism the system volume can be represented as infinite potential barrier at the walls of the container). More generally, $\lambda(t)$ can be any external field. For adiabatic thermodynamic process the question asked in the previous paragraph is: what are the conditions on $\lambda(t)$ such that the resulting thermodynamic process is quasi-static?

Let us recall that thermodynamics deals with systems possessing the property of relaxation to equilibrium. The relaxation can be characterized by a finite time τ_{rel} such that after that time, at fixed external conditions, the system is in equilibrium whatever its initial condition was. The time-scale τ_{rel} allows to formulate the answer to the questions asked above: quasi-static process is a process that takes place at a time-scale T much larger than τ_{rel}. Let us explain the answer using the example of adiabatic thermodynamic process. The time-scale T of the process can be introduced by setting $\lambda(t) = f(t/T)$ where $f(t)$ varies at a scale of order one. During a separation time-scale Δt obeying $\tau_{rel} \ll \Delta t \ll T$ (cf. the previous section), the Hamiltonian of the system can be considered constant due to $\Delta t \ll T$. On the other hand, due to $\tau_{rel} \ll \Delta t$ during the time-scale Δt the system relaxes to the equilibrium of a closed system which Hamiltonian is given by $H[\boldsymbol{p}, \boldsymbol{q}, \lambda(t)]$ "frozen" at the local time. In other words, during the process the system is all the time in equilibrium with parameters of equilibrium (such as the system energy $E(t)$ or $\lambda(t)$ itself) being functions of time that change at a time-scale T. On the other hand, if we dealt with a fast process with $T < \tau_{rel}$ the system would be locally out of equilibrium and the process would not be quasi-static.

Much insight into the nature of adiabatic thermodynamic process can be reached for ergodic systems. Ergodic systems are closed systems which phase space trajectory wanders over the whole surface $H(\boldsymbol{p}, \boldsymbol{q}) = const$ so that the ergodic theorem holds:

$$\lim_{T_0 \to \infty} \frac{1}{T_0} \int_0^{T_0} f(\boldsymbol{p}, \boldsymbol{q}, t) dt = K\delta(H(\boldsymbol{p}, \boldsymbol{q}) - E_0), \tag{20}$$

where K is the normalization factor,

$$K^{-1} = \int d\boldsymbol{p} d\boldsymbol{q} \delta(H(\boldsymbol{p}, \boldsymbol{q}) - E_0), \tag{21}$$

E_0 is the conserved energy of the system and $f(\boldsymbol{p}, \boldsymbol{q}, t) = \delta(\boldsymbol{p} - \boldsymbol{p}(t))\delta(\boldsymbol{q} - \boldsymbol{q}(t))$ is the exact distribution function of the system. The above microcanonical distribution implies the usual relation for the time-average of a function $F[\boldsymbol{p}(t), \boldsymbol{q}(t)]$ of the phase space variables:

$$\lim_{T_0 \to \infty} \frac{1}{T_0} \int_0^{T_0} F(\boldsymbol{p}(t), \boldsymbol{q}(t)) dt = \lim_{T_0 \to \infty} \frac{1}{T_0} \int_0^{T_0} dt \int d\boldsymbol{p} d\boldsymbol{q} F(\boldsymbol{p}, \boldsymbol{q}) f(\boldsymbol{p}, \boldsymbol{q}, t) = K \int d\boldsymbol{p} d\boldsymbol{q} F(\boldsymbol{p}, \boldsymbol{q}) \delta(H(\boldsymbol{p}, \boldsymbol{q}) - E_0),$$

where it is assumed that the orders of the integration and the limit are interchangeable. For ergodic systems the relaxation time τ_{rel} is given by the characteristic value of T_0 at which the limit in Eq. (20) saturates,

$$\frac{1}{\tau_{rel}} \int_0^{\tau_{rel}} f(\boldsymbol{p}, \boldsymbol{q}, t) dt \approx K\delta(H(\boldsymbol{p}, \boldsymbol{q}) - E_0), \tag{22}$$

where the approximate equality is considered in the sense that integrals of both sides with an arbitrary smooth function $F(\boldsymbol{p}, \boldsymbol{q})$ are approximately equal. The time τ_{rel} can be seen as a characteristic time at which the system trajectory "fills" the surface $H(\boldsymbol{p}, \boldsymbol{q}) = const$. Now if we consider adiabatic thermodynamic process for an ergodic system we have

$$\frac{1}{\Delta t} \int_t^{t+\Delta t} f(\boldsymbol{p}, \boldsymbol{q}, t') dt' \approx K(t)\delta[H(\boldsymbol{p}, \boldsymbol{q}, \lambda(t)) - E(t)], \quad K^{-1}(t) = \int d\boldsymbol{p} d\boldsymbol{q} \delta(H(\boldsymbol{p}, \boldsymbol{q}) - E(t)), \tag{23}$$

where $E(t)$ is the thermodynamical energy of the system. Indeed, by definition of τ_{rel} for ergodic system, due to $\Delta t \gg \tau_{rel}$ the limit above should saturate at the microcanonical distribution of the system with the locally constant (by $\Delta t \ll T$) Hamiltonian $H[\boldsymbol{p}, \boldsymbol{q}, \lambda(t)]$. Returning to the general case, the conclusion is that a process is quasi-static if it takes place at a time-scale much larger than the relaxation time of the system, $T \gg \tau_{rel}$. During the process thermodynamic variables like $E(t)$ and $V(t)$ vary at a time scale much larger than τ_{rel}. Time variation of other thermodynamic functions can be inferred from the equation of state, like in the relation for the pressure $p(t) = p[E(t), V(t)]$, where the function $p(E, V)$ describes the equation of state of the system.

We conclude that thermodynamics implies that when a macroscopic system undergoes a slow process, one can introduce a limited number of variables which obey a closed dynamics. These variables by themselves change slowly, in other words they are *slow variables*. Could we guess from mechanics that for a macroscopic system the consideration of slow processes (such as those occurring at the human time-scale) allows to perform an overwhelming reduction in the number of variables and to perform a reduced description of the system? To approach this question, let us consider again an adiabatic thermodynamic process. This choice is the simplest since the system is governed by a closed Hamiltonian dynamics during the process. Taking for definiteness the case where λ is the volume, at each moment of time we may characterizethe system by two thermodynamic state variables: the volume $V(t)$ and the energy $E(t)$. These variables, however, are not independent: the entropy S is conserved in the adiabatic process and thus the equation

$$S\left[V(t), E(t)\right] = S_0, \quad S_0 \equiv S\left[V(0), E(0)\right], \tag{24}$$

should hold. In particular, if one knows the equation of state in the form $S = S(E, V)$ the above allows to determine the evolution of system energy for given evolution of the volume. Thus thermodynamics leads to the conclusion that a thermally insulated system, characterized by a Hamiltonian with a slowly varying volume, has an approximate integral of motion which is a function of the system energy and volume only.

The above statement on the existence of an approximate integral of motion is a clear statement about the mechanics of the system. Somehow it means that a macroscopic system should have a dynamical property which is not so evident from the viewpoint of dynamics itself. Could we return to the dynamical description and rederive the conclusion? In general this is very hard - it is just one of the cases where the emergent laws (laws of thermodynamics) lead to a conclusion that would be very hard to derive from the laws at the more fundamental level. However, for ergodic systems, it is possible to deal with the question. In the derivation below we suppress the small parameter of the expansion ϵ which is the (slow) rate of the macroscopic process of the volume variation, $V(t) \equiv \tilde{f}(\epsilon t)$.

Let us study the time-derivative of $E(t)$ for an ergodic system. We have

$$\frac{dE}{dt} = \frac{d}{dt} H\left[\boldsymbol{p}(t), \boldsymbol{q}(t), V(t)\right] = \frac{\partial H}{\partial V}\left[\boldsymbol{p}(t), \boldsymbol{q}(t), V(t)\right] \frac{dV}{dt}, \tag{25}$$

where we used that $\boldsymbol{p}(t)$ and $\boldsymbol{q}(t)$ obey Hamilton equations of motion. Let us note that $E(t)$ changes at least at the time-scale of $V(t)$, so that $E(t) \approx \langle E \rangle_{\Delta t}(t)$. This allows us to write

$$\frac{dE}{dt} \approx \frac{dV}{dt} \int_t^{t+\Delta t} \frac{dt'}{\Delta t} \frac{\partial H}{\partial V}\left[\boldsymbol{p}(t'), \boldsymbol{q}(t'), V(t)\right], \tag{26}$$

where we do not account in the averaging for the factors that vary at the time-scale $T \gg \Delta$. Now we can use the ergodic theorem to write

$$\frac{dE}{dt} = \frac{dV}{dt} K(t) \int d\boldsymbol{p} d\boldsymbol{q} \frac{\partial H}{\partial V}\left[\boldsymbol{p}, \boldsymbol{q}, V(t)\right] \delta\left[H\left(\boldsymbol{p}, \boldsymbol{q}, \lambda(t)\right) - E(t)\right]. \tag{27}$$

The above equation allows an equivalent rewriting as

$$\Phi\left[E(t), V(t)\right] = const, \tag{28}$$

where $\Phi(E, V)$ is the volume of the phase space with energy smaller than E, at the system volume V,

$$\Phi(E, V) = \int \frac{d\boldsymbol{p} d\boldsymbol{q}}{(2\pi\hbar)^{3N}} \theta\left[E - H(\boldsymbol{p}, \boldsymbol{q}, V)\right]. \tag{29}$$

Above N is the number of degrees of freedom of the system and the factor $(2\pi\hbar)^{3N}$ is introduced for convenience in the following. We have

$$\frac{d\Phi(E(t), V(t))}{dt} = \frac{dE}{dt} \int \frac{d\boldsymbol{p} d\boldsymbol{q}}{(2\pi\hbar)^{3N}} \delta\left(E - H(\boldsymbol{p}, \boldsymbol{q}, V)\right) - \frac{dV}{dt} \int \frac{d\boldsymbol{p} d\boldsymbol{q}}{(2\pi\hbar)^{3N}} \frac{\partial H}{\partial V}\left[\boldsymbol{p}, \boldsymbol{q}, V(t)\right] \delta\left[H(\boldsymbol{p}, \boldsymbol{q}, V(t)) - E(t)\right] = 0,$$

where we used Eqs. (23) and (27). Any other parameter in the Hamiltonian could be used above instead of V. Thus we have shown that when a parameter in the Hamiltonian of an ergodic system changes at a time-scale much larger than τ_{rel} then the phase space volume Φ is approximately constant. In mechanics quantities that remain approximately constant under slow transformation of a parameter in the Hamiltonian are called adiabatic invariants. Since Φ is constant only for ergodic systems, it is referred to as ergodic adiabatic invariant. Its conservation can be traced to the

Liouville theorem stating that the volume in the phase space is preserved under the motion governed by the Hamilton equations. As a result, the initial microcanonical distribution, which is singular at the surface of constant energy, is transformed by the considered process into another microcanonical distribution also singular at some surface in such a way that the volume enclosed by the surface is preserved. This preservation is tantamount to Eq. (28).

Equations (24) and (28) suggest that for ergodic systems entropy is a function of Φ. The appropriate definition is (in this course we shall set $k_B = 1$):

$$S(E, V) = \ln \Phi(E, V). \tag{30}$$

For large systems the above definition is equivalent to the famous Boltzmann formula $S = \ln W$ where $W \approx \Delta E \partial_E \Phi$ is the number of states available to the system with energy in the window $(E, E + \Delta E)$. The equivalence follows from $W \sim \exp[Es(E/V)]$ leading to $\Phi \sim \exp[Es(E/V)]$ with difference in prefactors giving subleading corrections (roughly logarithm of a volume of a ball in a high-dimensional space is close to the logarithm of the volume of a spherical layer with the same radius).

Thus for a thermally insulated system, entropy S defined by Eq. (30) is a quantity that changes slower than macroscopic parameters of energy and volume. When the system is not thermally insulated, one can expect S to vary at the time-scale of heat exchange which is the same as the time-scale of variations of the energy and the volume. In other words, this allows to expect on the basis of mechanics that S is a slow variable in thermodynamic processes.

The idea to use the definition (30) for the entropy and to approach the equilibrium statistical mechanics on the basis of adiabatic invariants was introduced by Hertz in 1910. Whilst the approach was appreciated by Einstein, it remains a less known one today. To demonstrate the utility of the above definition we have to examine the second law of thermodynamics with its help. The latter consists essentially of two parts: the statement that there exists an integrating factor $1/T$ such that $\delta Q/T$ is an exact differential dS, and the principle of entropy increase for a closed system. Let us first address the former part of the second law.

A. Generalized Helmholtz theorem

To construct the dynamical version of the first part of the second law we must first construct the temperature T. A natural definition of T is provided by the equipartition theorem that states that for any system which Hamiltonian is the sum of the kinetic energy E_{kin} and the potential energy having no dependence on particle velocities, one has

$$T = \frac{2}{3N} \lim_{T_0 \to \infty} \frac{1}{T_0} \int_0^{T_0} E_{kin}(t) dt. \tag{31}$$

For ergodic system T allows a simple explicit expression:

$$T = \frac{2}{3N} K \int d\boldsymbol{p} d\boldsymbol{q} \, \delta \left(E - H(\boldsymbol{p}, \boldsymbol{q}, V) \right) E_{kin} = \frac{1}{3N} K \int d\boldsymbol{p} d\boldsymbol{q} \, \delta \left(E - H(\boldsymbol{p}, \boldsymbol{q}, V) \right) \boldsymbol{p} \cdot \frac{\partial H}{\partial \boldsymbol{p}}$$

$$= -\frac{1}{3N} K \int d\boldsymbol{p} d\boldsymbol{q} \boldsymbol{p} \cdot \frac{\partial}{\partial \boldsymbol{p}} \theta \left(E - H(\boldsymbol{p}, \boldsymbol{q}, V) \right) = K \Phi (2\pi\hbar)^{3N}, \tag{32}$$

where in the last line we performed integration by parts. Noting from Eq. (21) that $K^{-1} = (2\pi\hbar)^{3N} \partial_E \Phi$ we may rewrite the above expression as the fundamental thermodynamic relation $T^{-1} = \partial_E S$ with S defined by Eq. (30). This gives another confirmation of the adequacy of the latter definition.

Let us now show that $1/T$ is an integrating factor for $dE + pdV$ by showing explicitly that $(dE + pdV)/T$ is a differential of a function of state. This function is nothing but S defined in Eq. (30). We have

$$dS = \frac{\partial S}{\partial E} dE + \frac{\partial S}{\partial V} dV = \frac{dE}{T} + \frac{\partial S}{\partial V} dV, \tag{33}$$

where

$$\frac{\partial S}{\partial V} = -\frac{1}{\Phi} \int \frac{d\boldsymbol{p} d\boldsymbol{q}}{(2\pi\hbar)^{3N}} \delta \left(E - H(\boldsymbol{p}, \boldsymbol{q}, V) \right) \frac{\partial H}{\partial V} [\boldsymbol{p}, \boldsymbol{q}, V] = \frac{p}{\Phi K (2\pi\hbar)^{3N}} = \frac{p}{T}. \tag{34}$$

In the last line we used the definition of pressure and ergodicity:

$$p = -\lim_{T_0 \to \infty} \frac{1}{T_0} \int_0^{T_0} \frac{\partial H}{\partial V} [\boldsymbol{p}(t), \boldsymbol{q}(t), V] \, dt = -K \int d\boldsymbol{p} d\boldsymbol{q} \, \delta \left(E - H(\boldsymbol{p}, \boldsymbol{q}, V) \right) \frac{\partial H}{\partial V} [\boldsymbol{p}, \boldsymbol{q}, V]. \tag{35}$$

The above proves that for ergodic systems $(dE + pdV)/T$ is an exact differential, $(dE + pdV)/T = dS$ with S given by Eq. (30). The last statement has the name of generalized Helmholtz theorem as it generalizes an analogous relation for one-dimensional systems that was derived by Helmholtz. The crucial part in the above derivation is the representation (32) for the temperature.

B. The second law of thermodynamics

Once we have provided a mechanical definition for the entropy, it is natural to inquire if it can reproduce the statement of the second law of thermodynamics that the entropy of the closed system never decreases and it is maximal in equilibrium. And obviously, it is not - for fixed energy S defined by Eq. (30) is always constant. However, this does not yet signify that one cannot approach the second law with the definition (30). The reason is that once one tries to approach the second law from the view-point of dynamics of a system with a finite number of degrees of freedom, different formulations of the second law need no longer be equivalent. They only become so in the limit of the infinite number of degrees of freedom. Here we will show that a a particular formulation of the second law does hold for Eq. (30) while at home you are invited to demonstrate another formulation using similar techniques.

The Clausius principle of the entropy increase states that for a thermally isolated system which begins and ends in an equilibrium state, the entropy of the final state is greater than or equal to that of the initial state, where the equality holds if the process is quasi-static. The statement was already verified for quasi-static processes for Eq. (30), now we generalize. Although one can continue using the framework of classical statistical mechanics, we now deal with the question within quantum statistical mechanics - both for illustrative purposes and to provide methods for solving the problem set.

We first introduce the quantum version of the definition (30). We note that Bohr-Sommerfeld quantization conditions suggest that Φ can be approximated by $N + 1/2$, where N is the number of states with energy smaller than E. To introduce the quantum version of (30), we define the time-dependent quantum number operator

$$\hat{N}(t) \equiv \sum_{k=0}^{K_{tot}} k|k,t><k,t|, \tag{36}$$

where K_{tot} is the total (possibly infinite) number of the energy levels and $|k,t>$ are the eigenstates of the Hamiltonian, $\hat{H}[\boldsymbol{p}, \boldsymbol{q}, \lambda(t)] = \sum_{k=0}^{K_{tot}} \epsilon_k(t)|k,t><k,t|$. For the above definition to provide the correct quantum number at any t, it will be assumed that energy levels are non-degenerate and there is no level crossing, i.e. $\epsilon_k(t)$ remain ordered at any t. We now define the quantum entropy operator

$$\hat{S}(t) \equiv \ln\left(\hat{N}(t) + \frac{1}{2}\right). \tag{37}$$

In fact, the factor $1/2$ is not needed for the following proof of the Clausius principle but we shall keep it to be in accord with the original proposition by Campisi. Note that in contrast to the Hamiltonian's spectrum, the spectrum of $\hat{S}(t)$ is the same at any t. The Campisi definition is alternative to von Neumann's one $-Tr\hat{\rho}\ln\hat{\rho}$, where $\hat{\rho}(t)$ is the density matrix. The von Neumann entropy would remain constant and would not satisfy the Clausius principle. Since the system is initially in equilibrium, $\hat{\rho}(0)$ commutes with $\hat{H}(0)$ and can be written as $\hat{\rho}(0) = \sum_{k=0}^{K_{tot}} p_k|k,0><k,0|$. We make an important assumption that the eigenvalues of $\hat{\rho}(0)$ constitute a non-increasing function of the energy level number:

$$p_m \geq p_n, \quad if \quad m < n. \tag{38}$$

In particular the above equation holds if the initial distribution is the Gibbs distribution $p_k \propto \exp[-\epsilon_k/T]$ (this is the case if the system was put in contact with a thermal bath at temperature T and later decoupled from the bath). We now pass to the demonstration of the Clausius principle for a process that starts at $t = 0$ and ends at $t = t_f$. Variation in the Hamiltonian causes a transition between the quantum states according to the transition probabilities

$$|a_{kn}(t_f)|^2 = |<n,t_f|\hat{U}(t_f)|k,0>|^2, \tag{39}$$

where $\hat{U}(t)$ is the unitary time evolution operator. As a result the density matrix evolves to $\hat{\rho}(t_f) = \hat{U}(t_f)\hat{\rho}(0)\hat{U}^+(t_f)$. Let us consider the change in the expectation value of the entropy operator,

$$S_f - S_0 = Tr\left[\hat{\rho}(t_f)\hat{S}(t_f) - \hat{\rho}(0)\hat{S}(0)\right]. \tag{40}$$

Using that the spectrum of $\hat{S}$ is always the same we have

$$Tr\hat{\rho}(t_f)\hat{S}(t_f) = \sum_{n=0}^{K_{tot}} <n,t_f|\hat{\rho}(t_f)|n,t_f> \ln(n+1/2) = \sum_{n=0}^{K_{tot}} p'_n \ln(n+1/2) \tag{41}$$

where the probability $p'_n = <n, t_f | \hat{\rho}(t_f) | n, t_f>$ for the system to be found in the state $|n, t_f>$ is the sum $p'_n = \sum_{k=0}^{K_{tot}} p_k |a_{kn}(t_f)|^2$ describing the contributions of transitions from initial states $|k, 0>$ [formally this follows from $\hat{\rho}(t_f) = \hat{U}(t_f)\hat{\rho}(0)\hat{U}^+(t_f)$]. Thus we can represent Eq. (40) as

$$S_f - S_0 = \sum_{n=0}^{K_{tot}} (p'_n - p_n) \ln(n + 1/2). \tag{42}$$

We now use the summation by parts formula for the series,

$$\sum_{n=0}^{N} a_n b_n = a_N \sum_{n=0}^{N} b_n - \sum_{m=0}^{N-1} [a_{m+1} - a_m] \sum_{n=0}^{m} b_n. \tag{43}$$

The proof of the above formula can be obtained by representing b_n as a "derivative", $b_n = B_n - B_{n-1}$ where $B_n \equiv \sum_{k=0}^{n} b_k$ for $n \geq 0$ and $B_{-1} = 0$. The resulting series $\sum_{n=0}^{N} a_n(B_n - B_{n-1})$ can be written as $\sum_{n=0}^{N} [a_n B_n - a_{n-1} B_{n-1}] - \sum_{n=0}^{N} [a_n - a_{n-1}] B_{n-1} = a_N B_N - \sum_{n=0}^{N-1} [a_{n+1} - a_n] B_n$ equivalent to the formula above. Using Eq. (43) and the conservation of probability in the form $\sum_{n=0}^{K_{tot}} (p'_n - p_n) = 0$, we may rewrite Eq. (42) as

$$S_f - S_0 = \sum_{m=0}^{K_{tot}} \ln\left(\frac{m + 3/2}{m + 1/2}\right) \sum_{n=0}^{m} (p_n - p'_n). \tag{44}$$

We have

$$\sum_{n=0}^{m} (p_n - p'_n) = \sum_{n=0}^{m} p_n - \sum_{n=0}^{m} \sum_{i=0}^{K_{tot}} p_i |a_{in}(t_f)|^2 = \sum_{n=0}^{m} p_n \left(1 - \sum_{i=0}^{m} |a_{in}(t_f)|^2\right) - \sum_{n=0}^{m} \sum_{i=m+1}^{K_{tot}} p_i |a_{in}(t_f)|^2. \tag{45}$$

The transition probabilities obey $\sum_{k=0}^{K_{tot}} |a_{kn}(t_f)|^2 = \sum_{n=0}^{K_{tot}} |a_{kn}(t_f)|^2 = 1$ so that $1 - \sum_{i=0}^{m} |a_{in}(t_f)|^2 \geq 0$. Then, combining the equation above and the ordering of probabilities (38), we find

$$\sum_{n=0}^{m} (p_n - p'_n) \geq p_m \sum_{n=0}^{m} \left(1 - \sum_{i=0}^{m} |a_{in}(t_f)|^2\right) - p_m \sum_{n=0}^{m} \sum_{i=m+1}^{K_{tot}} |a_{in}(t_f)|^2 = m p_m - p_m \sum_{n=0}^{m} \sum_{i=0}^{K_{tot}} |a_{in}(t_f)|^2 = 0. \tag{46}$$

It follows that the RHS of Eq. (44) is a sum of non-negative terms and we have obtained that

$$S_f \geq S_0. \tag{47}$$

Clearly the equality occurs only if $p'_n = p_n$. This is just the case of an adiabatic thermodynamic process where no transitions occur between the states with different quantum number so that $|a_{in}(t_f)|^2 = \delta_{in}$ and $S_f = S_0$ holds. Note that, like the Clausius principle itself, the above derivation does not claim that the expectation value of $\hat{S}$ is a monotonically increasing function of time. It can still be true that $S_1 < S_2$ for $t_1 > t_2 > 0$ despite $S_1 > S_0$ and $S_2 > S_0$. What distinguishes the $t = 0$ moment here is that $\hat{\rho}(t = 0)$ is diagonal in the energy representation, while $\hat{\rho}(t)$ generally not.

Whenever one comes across a mechanical proof that the expectation value of some operator grows monotonically, the question comes what breaks the time-reversal symmetry. In our case, the symmetry is broken by the assumption of the ordering of probabilities (38). In particular, if the assumption would be reversed to $p_m < p_n$, the converse conclusion of *decrease* of entropy would be obtained. This is in accord with the fact that $p_m < p_n$ corresponds to inverse population and negative temperature states that do not occur naturally.

C. Summary

To summarize this section, we have seen that combining the assumption of ergodicity with the averaging method, one can reach a rather deep insight into the laws of thermodynamics starting with the microscopic dynamics. The method of thermodynamics as it is viewed dynamically is to introduce a certain set of variables that change slowly on the macroscopic time-scale. This is in contrast to immediate dynamical variables of the system, such as momenta or coordinates of the particles, which undergo rapid, "chaotic" changes. The variables in question are not just generalized coordinates, that is they are not necessarily functions on the phase space of the system (that is variables of the form

$F[\boldsymbol{p}(t), \boldsymbol{q}(t)]$, which are completely determined by the instantaneous state of the system). Rather these variables may be functionals of the *motion* of the system, that is their value may be determined by the whole trajectory of the system. An immediate example is pressure that from mechanical viewpoint represents a time-averaged force exerted on the system boundaries. During the course we shall encounter other types of such generalized characteristics of the system.

IV. BROWNIAN MOTION, LANGEVIN EQUATION AND EINSTEIN-STOKES RELATION

It is the core issue of the equilibrium statistical mechanics that when one looks at a macroscopic system in equilibrium then, while the system undergoes wild changes at the microscopic scale, at the macroscopic scale things are calm and smooth. One of the first observable effects of the invisible atomic motion that was discovered is Brownian motion. In 1829 a botanist Robert Brown observed fast irregular motions performed by tiny particles of plant pollen dispersed in water. This motion looked mysterious: one takes still water, puts small particles in it and they start to move. The resolution of the mystery with the help of the atomic hypothesis (contributed essentially by Einstein) was among the strongest arguments in favor of the existence of atoms before their more direct observation.

The theory of Brownian motion is one of the most important topics in non-equilibrium statistical physics because of its many extensions to situations where "Brownian particle" is not a particle at all but rather some collective property of a macroscopic system. Let us pass to this theory.

A. The setting of the problem

First we'd better address the question what a Brownian particle is. Normally, by a Brownian particle we mean a macroscopic particle immersed in a fluid. The particle size is supposed to be much larger than the correlation length beyond which the hydrodynamic description of the fluid motion applies (more details on this will be supplied below), while the particle mass is supposed to be larger than the mass of the particles comprising the fluid. Essentially by definition, a Brownian particle is a particle such that its velocity $\boldsymbol{v}(t)$ is a *slow* variable. Here slowness means that the relaxation time of the fluid τ_{rel} must be much smaller than the characteristic time-scale of the variations of velocity.

The slowness of the velocity variable can be illustrated by the following mechanical model of the Brownian motion. Within the model, the system "particle plus fluid" is described by the Hamiltonian

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{j>i} V(\mathbf{r}_i - \mathbf{r}_j) + \frac{p^2}{2M} + \sum_i U(\mathbf{r}_i - \mathbf{r}), \tag{48}$$

where $\mathbf{r}_i$, $\mathbf{p}_i$ are coordinates and momenta of N identical fluid particles with mass m while $\mathbf{r}$ and $\mathbf{p}$ are the coordinate and the momentum of the Brownian particle which mass M obeys $M \gg m$. Such properties as finite size of the Brownian particle could be accounted by setting $U(r) = 0$ at $r > a$ and $U(r) = \infty$ for $r < a$. Here a is the radius of the particle which is assumed spherical for simplicity.

The key to the solution of the problem is the inequality $m/M \ll 1$. The limit $m/M \to 0$ is the limit of an infinitely heavy Brownian particle. Such a particle would keep its velocity $\boldsymbol{v}$ constant despite the interaction with the fluid. After the relaxation time τ_{rel} the fluid will be in the stationary (equilibrium-like, see below) state corresponding to the particle moving in it with the speed $\boldsymbol{v}$. At a small but finite value of m/M the velocity $\boldsymbol{v}$ does change but it takes a characteristic time τ much larger than τ_{rel} before the velocity changes appreciably. As long as we consider values of m/M corresponding to $\tau \gg \tau_{rel}$, the fluid is in the local stationary state which parameter $\boldsymbol{v}(t)$ changes in time slowly.

To make the above less abstract consider the example where Brownian particle is a big ball colliding with small balls constituting a gas. In a gas one can speak of individual collisions of gas molecules with the Brownian particle. A single collision disturbs the velocity of the big ball insignificantly and it takes lots of collisions before there is an effect. As a result the gas reaches steady state corresponding to $\boldsymbol{v}(t)$ before the latter changes significantly. Note an important feature that the change in $\boldsymbol{v}(t)$ is caused by a *collective* effect of numerous collisions experienced by the particle. In this sense, the dynamics of $\boldsymbol{v}(t)$ is a collective property of the fluid.

Our purpose in this Section is to write down an effective equation for the dynamical variables of the Brownian particle, $\boldsymbol{r}$ and $\boldsymbol{p}$. This equation however will not correspond to the ordinary deterministic classical dynamics. To see that this is plausible, note that at the moment we introduce the Brownian particle into the fluid we know $\boldsymbol{r}$ and $\boldsymbol{p}$, but we do not know the coordinates and momenta of the fluid - they are random with the probability distribution described by the equilibrium statistical mechanics. Since the fluid can be in many different microscopic states, many possible trajectories of the particle can arise from macroscopically the same initial situation. As a result we can only

speak of probabilities of different trajectories. These are described by *random* dynamics where different forces have different probability weight. We now start the derivation.

B. The equation of motion of the Brownian particle, part I

The exact equation of motion of the Brownian particle is of course

$$\frac{d\boldsymbol{v}}{dt} = \frac{\boldsymbol{F}}{M}, \tag{49}$$

where $\mathbf{F}$ is the force exerted on the Brownian particle by the fluid. The main assumption of the theory of Brownian motion is that the relaxation time of the fluid τ_{rel} is much smaller than the characteristic time τ of variations of $\boldsymbol{v}(t)$. Thus performing the partial time averaging in the same way as we did in the previous sections we may write

$$\frac{d\boldsymbol{v}}{dt} = \frac{1}{M} \int_t^{t+\Delta t} \frac{dt'}{\Delta t} \boldsymbol{F}(t')|_{\boldsymbol{v}(t')=const=\boldsymbol{v}(t)}, \tag{50}$$

where $\tau_{rel} \ll \Delta t \ll \tau$ and the subscript signifies that the time average is taken at constant velocity of the particle, equal to $\boldsymbol{v}(t)$ in the whole time interval $(t, t+\Delta t)$. The above inequality uses only the $\Delta t \ll \tau$ part of $\tau_{rel} \ll \Delta t \ll \tau$. Using now that $\tau_{rel} \ll \Delta t$, we conclude that the above time average can be approximated by the time average over an infinite time interval (cf. the definition of the relaxation time in the previous Section), so that

$$\frac{d\boldsymbol{v}}{dt} \approx \frac{1}{M} \lim_{T_0 \to \infty} \int_t^{t+T_0} \frac{dt'}{T_0} \boldsymbol{F}(t')|_{\boldsymbol{v}(t')=const=\boldsymbol{v}(t)} \equiv \boldsymbol{F}_{av}[\boldsymbol{v}(t)], \tag{51}$$

Above $F_{av}(\boldsymbol{v})$ is the average force that acts on the Brownian particle that moves in the fluid at a constant velocity $\boldsymbol{v}$ (where some external forces are needed to sustain the motion, see below). The expression for the force $F_{av}(\boldsymbol{v})$ can be obtained within the framework of hydrodynamics.

C. The average component of the force

What is the state of the fluid provided there is a particle moving in it a constant velocity? To answer this question one can use the approximation of an infinite fluid, where the fluid is at rest at infinity while in the region near the particle the fluid is disturbed in some way. We understand that the state of the fluid cannot be a complete equilibrium: there must be a friction force exerted on the particle so that in contrast to equilibrium we must constantly supply energy to the system to keep the particle going. Still, the state of the fluid can be described as a generalization of the equilibrium state, the so-called local equilibrium state, where locally in space and time the fluid can be considered in equilibrium. The evolution of the local parameters of equilibrium is described by the equations of hydrodynamics that we will consider later in the course. Here we shall only use the result of the hydrodynamic analysis, the so-called Stokes law. This applies where the velocity is not too large so that the situation can be considered as a near-equilibrium one, as is the case of the theory of Brownian motion. The law expresses the friction force exerted by the fluid on the particle in terms of the "inner friction" coefficient of the fluid itself, the fluid viscosity η. Viscosity describes friction between two nearby layers of the fluid moving at different speeds. Inner forces in a fluid tend to equilibrate the velocities of the layers, which results in a friction force described by η. The Stokes law expresses the friction force on the particle in terms of η as s

$$\boldsymbol{F}_{av}(\boldsymbol{v}) = -6\pi a \eta \boldsymbol{v}. \tag{52}$$

As a result, Eq. (50) becomes

$$\frac{d\boldsymbol{v}}{dt} = -\frac{\boldsymbol{v}}{\tau}, \quad \tau = \frac{M}{6\pi a \eta}. \tag{53}$$

Let us stress that the above equation is the same whatever the initial microscopic state of the fluid was. Also if we put many Brownian particles at different positions and with different velocities, still, after a short transient in time, they all would satisfy the same equation (53). The time averaging wiped out all the details of the state of the fluid besides its viscosity. Let us note that though the linear friction law is very natural it is not trivial. For example, it would not hold in the two dimensional situation ("Brownian motion of a cylinder").

The above analysis provides a correct description of the velocity dynamics when the velocity is not too small. Nevertheless, there is an obvious problem with Eq. (53): at large times the particle velocity relaxes to $\boldsymbol{v} = 0$ and hence, in the end, no Brownian motion would occur! Moreover, $\boldsymbol{v} = 0$ would contradict thermodynamics which says that the final state of the system must be thermal equilibrium with the Maxwellian distribution of the particle velocity having the temperature of the fluid. Thus the lowest order approximation in the small parameter τ_{rel}/τ is not sufficient to describe the Brownian motion. The reason is that the leading order term in the expansion, $\langle F \rangle(\mathbf{v})$, vanishes exactly at $\mathbf{v} = 0$ where even small corrections to Eq. (53) become important. Thus we need to consider the corrections to the above equation

$$\frac{d\boldsymbol{v}}{dt} = -\frac{\boldsymbol{v}}{\tau} + \frac{\boldsymbol{f}(t)}{M}, \tag{54}$$

where $\boldsymbol{f}(t)$ describes the fluctuating component of the force providing corrections to the systematic component of the force given by friction.

D. The fluctuating component of the force

The properties of the fluctuating component of the force can be seen most clearly by considering the situation where due to external forces the Brownian particle is fixed at some position in the fluid. We now measure the force $\boldsymbol{f}(t)$ exerted by the fluid on the particle in much the same way as we would measure the force on the boundaries of the gas or liquid (here the surface of the Brownian particle is really a part of the gas boundary). We understand that on average the force is zero: all the bumps on one side of the particle will be eventually balanced by the bumps on the opposite side. So $\boldsymbol{f}(t)$ will have zero time average

$$\langle \boldsymbol{f}(t) \rangle \equiv \lim_{T_0 \to \infty} \int_t^{t+T_0} \frac{dt'}{T_0} \boldsymbol{f}(t') = 0. \tag{55}$$

Nevertheless, generally, $\boldsymbol{f}(t)$ deviates from its average at any given t. We say that it *fluctuates* near the average. If the particle would experience only the fluctuating component of the force $\boldsymbol{f}$, so that $d\boldsymbol{v}/dt = \boldsymbol{f}/M$, then the fluctuations of $\boldsymbol{f}$ near zero would have a non-trivial, important effect on $\boldsymbol{v}$, considered in detail in the next subsection. Thus we need to characterize $\boldsymbol{f}$ quantitatively. The most important characteristics of fluctuations is the correlation function, expressing the degree of correlation between the values of $\boldsymbol{f}$ at different times

$$\langle f_i(0) f_j(t) \rangle \equiv \lim_{T_0 \to \infty} \frac{1}{T_0} \int_{t_0}^{t_0+T_0} f_i(t') f_j(t' + t) dt'. \tag{56}$$

Above we noted the independence of the average on t_0: the fluid is in equilibrium state which is time shift invariant *on average*. A main assumption of the theory of Brownian motion is that $\boldsymbol{f}$ has a *finite correlation time* τ_{cor}. This means that $\langle f_i(0) f_j(t) \rangle$ is small at $t \gg \tau_{cor}$ so that roughly the values of the force $\boldsymbol{f}(t_1)$ and $\boldsymbol{f}(t_2)$ are independent whenever $|t_2 - t_1| \gg \tau_{cor}$. The decay of correlations is assumed sufficiently fast so that the integral $\int_0^\infty \langle f_i(0) f_j(t) \rangle dt$ converges and $\int_0^T \langle f_i(0) f_j(t) \rangle dt \approx \int_0^\infty \langle f_i(0) f_j(t) \rangle dt$ for any $T \gg \tau_{cor}$. The assumption of the finite correlation time of the force is very close to the assumption of the finite time of relaxation to the equilibrium and in fact we shall see via the fluctuation-dissipation theorem that there is a direct connection between the two assumptions. As in the case of the relaxation time, the finite correlation time can be argued for in ergodic systems and it is expected to hold normally.

The meaning of the assumption of finite relaxation time can be seen clearly in gases where the force exerted by the fluid on the surface of the fixed Brownian particle is a result of the sum of many collisions of individual gas particles against the surface. It is natural to expect that subsequent collisions of particles are independent of each other - dealing with about 10^{23} gas particles it is reasonable that every new gas particle coming to collide with the Brownian particle is not sensitive to the individual collisions of other particles that happened before. The latter assumption results in finiteness of the correlation time of $\boldsymbol{f}$. In fact, the assumption of independence of subsequent collisions is very similar to the Boltzmann "molecular chaos assumption", that we shall encounter in the derivation of Boltzmann equation, and it is a subtle assumption.

Below we shall assume that time averages of expressions involving the fluctuating force $\boldsymbol{f}(t)$, or the averages over the initial state of the fluid, can all be substituted by ensemble averages. The ensemble average signifies that $\boldsymbol{f}(t)$ is considered as a random vector function with a given statistics. In this sense $\boldsymbol{f}(t)$ is a random or stochastic process. The resulting dynamical equations with $\boldsymbol{f}$ on the RHS are called stochastic equations.

Let us briefly discuss stochastic processes. A stochastic process $\xi(t)$ is a collection of random variables labeled by a continuous index t. As any collection of random variables, $\xi(t)$ is characterized by the joint probability distribution function which here gives a probability weight to any given shape of $\xi(t)$. Thus the probability density of $\xi(t)$ is the probability density functional rather than function - it takes as an argument a function and assigns to it a number, the probability weight. Important characteristics of a random process are correlation functions which are moments of different orders: the average $\langle\xi(t)\rangle$, the pair correlation function $\langle\xi(t_1)\xi(t_2)\rangle$ or dispersion $\langle\langle\xi(t_1)\xi(t_2)\rangle\rangle \equiv \langle\xi(t_1)\xi(t_2)\rangle - \langle\xi(t_1)\rangle\langle\xi(t_2)\rangle$, the triple correlation function $\langle\xi(t_1)\xi(t_2)\xi(t_3)\rangle$ and so on. For the so-called stationary processes time shift invariance holds *on average* and the statistics of $\xi(t)$ and $\xi(t+t_0)$ are the same for any constant t_0. The correlation functions in this case depend only on differences of the time arguments. Finite correlation time τ_{cor} signifies that the values of the random process $\xi(t_1)$ and $\xi(t_2)$ are roughly independent at $|t_2-t_1| \gg \tau_{cor}$. For example, the dispersion decays rapidly at $|t_2 - t_1| \gg \tau_{cor}$ and $\int dt_2\langle\langle\xi(t_1)\xi(t_2)\rangle\rangle$ converges. The far reaching consequences of the assumption of finite correlation time are illustrated in the next subsection, where the connection with diffusion is demonstrated.

E. Motion driven by a random stationary process with a finite correlation time. Large time diffusive behavior

Let us consider an equation of the form

$$\dot{x} = \xi(t), \tag{57}$$

where $\xi(t)$ is a random stationary process (sometimes called noise) with a finite correlation time τ_{cor}. For simplicity we consider one-dimensional case - the generalization to higher dimensions is straightforward. Since average $\langle\xi\rangle$ could be eliminated by passing to the random variable $x(t) - t\langle\xi\rangle$, we assume with no loss that $\langle\xi\rangle = 0$. We designate the pair-correlation function by H so that $\langle\xi(t_1)\xi(t_2)\rangle = H(t_2 - t_1)$. The solution of Eq. (57) with $x(0) = x_0$ is

$$x(t) - x_0 = \int_0^t \xi(t')dt', \tag{58}$$

which gives

$$[x(t) - x_0]^2 = \int_0^t dt_1 dt_2 \xi(t_1)\xi(t_2) = 2\int_0^t dt_1 \int_0^{t_1} dt_2 \xi(t_1)\xi(t_2), \tag{59}$$

where we used that the integrand is symmetric. Taking the time derivative of the above equation and averaging over the statistics of ξ we obtain

$$\frac{d}{dt}\langle[x(t) - x_0]^2\rangle = 2\left\langle \int_0^t ds\,\xi(t)\xi(t - s)\right\rangle = 2\int_0^t ds\,H(s). \tag{60}$$

Above we noted that the pair correlation function of a stationary process is an even function of the time difference [using time shift invariance on average one has $H(-t) \equiv \langle\xi(0)\xi(-t)\rangle = \langle\xi(t)\xi(0)\rangle$]. At $t \gg \tau_{cor}$, the RHS of Eq. (60) saturates at a time-independent value producing

$$\frac{d}{dt}\langle[x(t) - x_0]^2\rangle \approx 2\int_0^\infty H(t')dt', \quad \langle[x(t) - x_0]^2\rangle \approx 2t\int_0^\infty H(t')dt', \quad t \gg \tau_{cor}. \tag{61}$$

We observe that even though $x(t)$ is driven by a stationary process, by itself it is not stationary - rather its amplitude grows proportionally to $\sqrt{t}$ on average. It should be stressed that $\langle x(t)\rangle$ is zero always, it is only the amplitude of the fluctuations that grows with time. Clearly, the amplitude growth is a result of the accumulation of effects of small fluctuations of ξ over.

The behavior described by Eq. (61) is a signature of diffusion. Consider the concentration of a tagged particle $P(x,t)$ that obeys the diffusion equation

$$\frac{\partial P}{\partial t} = D\frac{\partial^2 P}{\partial x^2}, \quad P(x, x_0, 0) = \delta(x - x_0), \tag{62}$$

where D is the diffusion coefficient and $P(x, x_0, 0)$ describes that the particle is initially at x_0. The mean squared displacement $\langle[x(t) - x_0]^2\rangle \equiv \int [x - x_0]^2 P(x, x_0, t)dx$ obeys

$$\frac{\partial}{\partial t}\int [x - x_0]^2 P(x, x_0, t) = D\int [x - x_0]^2 \frac{\partial^2 P(x, x_0, t)}{\partial x^2}dx = 2D, \tag{63}$$

where we integrated by parts twice and used that the diffusion equation conserves the total mass $\int P(x, x_0, t) = \int P(x, x_0, 0) = 1$. Integrating the above relation over time, we obtain the famous Einstein formula for one-dimensional diffusion that states that $\langle [x(t) - x_0]^2 \rangle = 2Dt$. Comparing Eq. (63) with Eq. (61), we find that the latter corresponds to diffusion with the diffusion coefficient

$$D = \int_0^\infty H(t)dt = \frac{1}{2} \int_{-\infty}^\infty H(t)dt. \tag{64}$$

The connection of Eq. (57) with the diffusion equation (62) is in fact stronger. We note that at $t \gg \tau_{cor}$ the RHS of Eq. (58) is roughly a sum of a large number t/τ_{cor} independent random variables. Indeed, if we choose Δt according to $\tau_{cor} \ll \Delta t \ll t$, assuming with no loss that $N = t/\Delta t \gg 1$ is an integer, then the summands in

$$\int_0^t \xi(t')dt' = \sum_{k=0}^{N-1} \int_{k\Delta t}^{(k+1)\Delta t} \xi(t')dt', \tag{65}$$

can easily be seen approximately independent due to $\tau_{cor} \ll \Delta t$. As a result, the probability distribution function of $x(t) - x_0$ is approximately Gaussian. Since a Gaussian distribution is determined uniquely by the average and the dispersion, then using $\langle x(t) \rangle = x_0$ and the results for $\langle [x(t) - x_0]^2 \rangle$, one finds the following Gaussian distribution for the probability distribution function (below PDF) of $x(t)$:

$$P(x, x_0, t) \equiv \langle \delta[x(t) - x] \rangle_{x(0)=x_0} = \left\langle \delta\left[x_0 + \int_0^t \xi(t')dt' - x\right] \right\rangle \approx \frac{1}{\sqrt{4\pi Dt}} \exp\left[-\frac{(x - x_0)^2}{4Dt}\right], \quad t \gg \tau_{cor}, \tag{66}$$

where the subscript stands for conditional averaging. We used the same notation for the PDF of $x(t)$ and the concentration in Eq. (62) on purpose - the above expression of is really the solution to Eq. (62), the so-called Green function of the heat equation. This is the first instance we encounter of an important connection between random dynamics and solutions to partial differential equations "of heat type".

If we lifted the assumption of zero average of ξ, then Eq. (66) would be changed to

$$P(x, x_0, t) \approx \frac{1}{\sqrt{4\pi Dt}} \exp\left[-\frac{(x - x_0 - \langle\xi\rangle t)^2}{4Dt}\right], \quad t \gg \tau_{cor}, \tag{67}$$

where $2D = \int \langle\langle \xi(0)\xi(t) \rangle\rangle dt$. We observe that at times much larger than the correlation time of the noise, all the fine details of the statistics of $\xi(t)$ in Eq. (57) are washed out - the statistics of $x(t)$ is determined only by $\langle\xi\rangle$ and the time integral of the dispersion $\langle\langle \xi(0)\xi(t) \rangle\rangle$ (sometimes called the *power* of the noise). This allows to substitute the dynamics (57) by the effective Langevin dynamics

$$\frac{dx}{dt} = \xi', \tag{68}$$

where ξ' is a Gaussian noise determined uniquely by the average $\langle\xi'\rangle = \langle\xi\rangle$ and the dispersion

$$\langle\langle \xi'(t_1)\xi'(t_2) \rangle\rangle = 2D\delta(t_2 - t_1), \quad D = \frac{1}{2} \int_{-\infty}^\infty \langle\langle \xi(0)\xi(t) \rangle\rangle dt. \tag{69}$$

At $t \gg \tau_{cor}$ the dynamics (68) leads to the same PDF of $x(t)$ as the original dynamics (57). Formally, the noise ξ' is obtained from ξ by taking the limit $\tau_{cor} \to 0$ at the constant power of the noise - note that $\int \langle\langle \xi(0)\xi(t) \rangle\rangle dt = \int \langle\langle \xi'(0)\xi'(t) \rangle\rangle dt$. A Gaussian noise which pair correlation function is a $\delta-$function, like the one in Eq. (69), is called a white noise (white because all frequencies are present in the noise spectrum, see subsection (IV I).

The generalization of the above analysis to vector case is straightforward. The vector $\boldsymbol{x}$ evolving in time according to

$$\frac{dx_i}{dt} = \xi_i(t), \tag{70}$$

will perform at large times diffusion with the diffusion coefficient

$$D = \frac{1}{6} \lim_{t \to \infty} \sum_{i=1}^3 \frac{\langle [x_i(t) - x_i(0)]^2 \rangle}{t} = \frac{1}{6} \int_{-\infty}^\infty \langle \boldsymbol{\xi}(0) \cdot \boldsymbol{\xi}(t) \rangle dt, \tag{71}$$

corresponding to the three-dimensional diffusion equation

$$\frac{\partial P}{\partial t} = D\nabla^2 P. \tag{72}$$

We conclude that if Brownian particle would experience only the fluctuating component of the force $\boldsymbol{f}$, then the typical value of its velocity would grow with time indefinitely. We now pass to consider the full dynamics of the Brownian motion.

F. The equation of motion of the Brownian particle, part II. Fluctuation-dissipation theorem

We are now ready to write down the complete effective dynamics of a Brownian particle. This is obtained by combining the large and small velocity asymptotic expression for the force in Eq. (49). We saw that at large velocities a linear friction term should describe the dynamics. On the other hand, at small velocities the friction is small and the fluctuating, zero-average component of the force becomes dominant. The overall dynamics takes into account the two components of the force and we have

$$\frac{d\boldsymbol{v}}{dt} = -\frac{\boldsymbol{v}}{\tau} + \frac{\boldsymbol{f}}{M}, \tag{73}$$

where $\boldsymbol{f}$ is a random force with zero average and a finite correlation time $\tau_{cor} \ll \tau$. The above equation can be seen as an effective form of Eq. (50) where the fluctuating term describes deviations of the finite time average on the RHS of Eq. (50) from its infinite time value $\boldsymbol{F}_{av}(\boldsymbol{v})$. Equation (73) is called Langevin equation [sometimes the term is reserved only for the case where $\boldsymbol{f}$ has $\delta-$function correlations in time like in Eq. (69)]. It substitutes the original random force F by another random force $\boldsymbol{f}$ which at first sight does not bring much. In fact, however, the decomposition in Eq. (73) along with the inequality $\tau_{cor} \ll \tau$ allows to solve the problem easily. It should be stressed that the statistics of $\boldsymbol{f}$ in Eq. (73) is independent of $\boldsymbol{v}$ - this is just the equilibrium statistics obtained in the auxiliary problem of fixed Brownian particle with $\boldsymbol{v} = 0$. One could say that the statistics of the fluctuating component of the force $\boldsymbol{F}$ has a regular limit at $v \to 0$ which is sufficient for Eq. (73), valid only at not too large $\boldsymbol{v}$. Moreover, the statistics of $\boldsymbol{f}$ is independent of the particle mass M - it depends solely on the particle size as one can be see from the previous discussion. The latter independence is essential because it guarantees that at a given particle size, the limit of large M necessarily leads to the separation of time-scales, $\tau \gg \tau_{cor}$. Indeed, while τ_{cor} is $M-$independent, τ grows with M indefinitely, see Eq. (53).

The two terms in Eq. (73) have opposite effects on the velocity. The friction tends to stop the particle and it dissipates any deviations of the particle velocity from zero. On the other hand, the fluctuating component of the force, via the accumulation of the effects of fluctuations with time, tends to increase the typical value of v indefinitely. Thus one expects a balance of the two forces at some intermediate value of velocity. This value of velocity is nothing but the thermal velocity $\sqrt{kT/M}$. Below the thermal velocity, at $v \ll \sqrt{kT/M}$, the friction in Eq. (73) is negligible, while at $v \gg \sqrt{kT/M}$ the fluctuating component of the force can be discarded and one can deal with the simple equation (53). Let us pass to the quantitative consideration. The solution of Eq. (73) reads

$$\boldsymbol{v}(t) = \boldsymbol{v}(0)e^{-t/\tau} + \frac{1}{M}\int_0^t e^{-(t-t')/\tau}\boldsymbol{f}(t')dt'. \tag{74}$$

We observe that the first term in the above expression decays with time and it becomes small exponentially at $t \gg \tau$. In particular, the initial value of velocity is forgotten within a characteristic time τ - at $t \gg \tau$ the information on the initial velocity is essentially lost. This irreversibility is a natural effect of friction - if we set a particle in motion in a fluid then, due to the friction, the particle will eventually stop and the system will look the same whatever the initial velocity was. Thus at large times the first term in the RHS of Eq. (79) can be discarded and we obtain

$$\boldsymbol{v}(t) = \frac{1}{M}\int_0^t e^{-(t-t')/\tau}\boldsymbol{f}(t')dt' \approx \frac{1}{M}\int_{-\infty}^t e^{-(t-t')/\tau}\boldsymbol{f}(t')dt', \quad t \gg \tau, \tag{75}$$

where we extended the lower limit of integration to $-\infty$ using the exponential decay factor. The above equation defines a stationary random process $\boldsymbol{v}(t)$ thus showing that $\boldsymbol{v}(t)$ relaxes to a steady state within relaxation time τ. One can see that $\boldsymbol{v}(t)$ is a Gaussian random process. Indeed, since $\exp[-(t-t')/\tau]$ changes at a time-scale τ, then we may write

$$\int_{-\infty}^t e^{-(t-t')/\tau}\boldsymbol{f}(t')dt' \approx \int_{-\infty}^t e^{-(t-t')/\tau}\langle\boldsymbol{f}(t')\rangle_{\Delta t}dt', \tag{76}$$

where $\langle \boldsymbol{f}(t') \rangle_{\Delta t}$ is $\boldsymbol{f}(t')$ averaged over a time interval Δt with $\tau_{cor} \ll \Delta t \ll \tau$. We observe that $\langle \boldsymbol{f}(t') \rangle_{\Delta t}$ is a sum of a large number of independent random variables due to $\tau_{cor} \ll \Delta t$. Since linear operations over Gaussian variables preserve Gaussianity, then we conclude that $\boldsymbol{v}(t)$ is Gaussian. The Gaussianity of $\boldsymbol{v}(t)$ could be anticipated based on our discussion of the behavior of a Brownian particle in a gas: appreciable changes in the particle velocity result only from summing the impacts of many collisions of the particle with the molecules of the gas. If the latter collisions are independent then the velocity is given by the sum of a large number of independent random variables and hence it must be Gaussian. It follows that the single time distribution of $\boldsymbol{v}(t)$ is determined uniquely by $\langle \boldsymbol{v} \rangle = 0$ and the correlation matrix $\langle v_i(t) v_j(t) \rangle$ given by

$$\langle v_i v_j \rangle = \frac{2}{M^2} \int_{-\infty}^{t} dt_2 \int_{-\infty}^{t_2} dt_1 e^{-(2t-t_1-t_2)/\tau} C_{ij}(t_2 - t_1), \tag{77}$$

where we introduced $C_{ij}(t) \equiv \langle f_i(0) f_j(t) \rangle$ and used that the integrand is a symmetric function of t_1 and t_2. The function $C_{ij}(t_2 - t_1)$ confines the difference $t_2 - t_1$ to $t_2 - t_1 \lesssim \tau_{cor} \ll \tau$ so that $\exp[-(2t-t_1-t_2)/\tau] \approx \exp[-2(t-t_2)/\tau]$. Introducing $s = t_2 - t_1$ we have

$$\langle v_i v_j \rangle = \frac{2}{M^2} \int_{-\infty}^{t} dt_2 e^{-2(t-t_2)/\tau} \int_{0}^{\infty} C_{ij}(s) ds = \frac{\tau}{M^2} \int_{0}^{\infty} \langle f_i(0) f_j(t) \rangle dt. \tag{78}$$

On the other hand, we know from thermodynamics what the limiting distribution of $\boldsymbol{v}$ must be Maxwellian, that is $\boldsymbol{v}$ is Gaussian indeed with zero average and

$$\langle v_i v_j \rangle = \frac{\delta_{ij} kT}{M}. \tag{79}$$

Comparing Eqs. (81) and (79), we conclude that the fluctuating component of the force correlation function must obey

$$\frac{\tau}{M} \int_{0}^{\infty} \langle f_i(0) f_j(t) \rangle dt = \delta_{ij} kT. \tag{80}$$

Taking the trace of the above equation we find that the macroscopic friction coefficient obeys

$$\frac{1}{\tau} = \frac{1}{6MkT} \int_{-\infty}^{\infty} \langle \boldsymbol{f}(0) \cdot \boldsymbol{f}(t) \rangle dt. \tag{81}$$

Finally, using Eq. (53) we may also write

$$\eta = \frac{1}{36\pi a kT} \int_{-\infty}^{\infty} \langle \boldsymbol{f}(0) \cdot \boldsymbol{f}(t) \rangle dt. \tag{82}$$

Note that the mass cancelled in the last expression as it should: η is a property of the fluid and not the particle and thus it must not depend neither on M, nor on a. In particular, we conclude that the force correlation function must be such that the above expression is $a-$independent. The above relation is not the most convenient expression for η in terms of the equilibrium fluctuations of the system, though it is conceptually the simplest one. Other expression for η will be considered later.

Equations (81)-(82) constitute a very important result, the so-called fluctuation-dissipation theorem (below the FDT). The content of the fluctuation-dissipation theorem is a relation between two properties of the system: dissipation coefficient and system fluctuations in the equilibrium. The dissipation coefficient describes system relaxation to equilibrium. An example of a dissipation coefficient is the friction coefficient $1/\tau$ in Eq. (53). If we introduce a particle in the fluid with a finite velocity then, after a while, this velocity disappears due to friction and kinetic energy of the particle dissipates into heat. Fluctuation-dissipation theorem tells us that fluctuations and dissipation in macroscopic systems are essentially equivalent. One direction is clear: if there are fluctuations of the macroscopic variables from their equilibrium values then there must be a related dissipation that would enforce the return to equilibrium. Another direction is less obvious: if after a deviation a macroscopic variable returns to its specific equilibrium value why should this imply that there are fluctuations in the equilibrium? To see the implication, note that absence of fluctuations signifies infinite memory. On the other hand, dissipation signifies absence of memory or finite correlation time (we have seen already that finite correlation time is a crucial assumption for our consideration of the Brownian motion).

The theorem shows that the kinetic coefficients of friction and viscosity, that characterize the system relaxation to equilibrium and thus a non-equilibrium dynamics, are determined by the equilibrium properties of the system. The

latter include both the amplitude A of the equilibrium fluctuations of $\boldsymbol{f}$ and their correlation time τ_{cor}: the integral in Eq. (81) can be estimated as $A^2\tau_{cor}$. For example, the larger A is, the larger momentum is transferred to the Brownian particle in each elementary interaction with the fluid, and hence the faster deviations of $\boldsymbol{v}$ from zero are damped or the smaller τ is. Note that for the FDT to be meaningful it is necessary that equilibrium fluctuations have finite correlation time, so that there is forgetting of initial fluctuations. Such forgetting intuitively reflects the same property of the system as the dissipation coefficient and the FDT formalizes this intuition. We shall say more on this below in the discussion of the Onsager principle. Finally, note that in the end, both τ and $\boldsymbol{f}$ arise from the decomposition of the same molecular force $\boldsymbol{F}$ and thus a connection between them is natural.

G. The connection between diffusion and finite correlation time of particle velocity. Einstein-Stokes relation.

We saw above that the stochastic dynamics of the form $\dot{x} = \xi(t)$, where $\xi(t)$ is a random process with a finite correlation time τ_{cor} leads to the diffusive behavior of $x(t)$ at $t \gg \tau_{cor}$. Applying this result in the most straightforward way, we conclude that if a particle velocity in the relation

$$\frac{d\boldsymbol{x}}{dt} = \boldsymbol{v}(t), \tag{83}$$

has a finite correlation time, then, at large times, the particle performs diffusion in the real space. It should be stressed that the result applies in many different situations. For example it is applicable to the situation when the particle moves in a fluid which motion is turbulent - in that case $\boldsymbol{v}(t)$ should also be considered as a random process with a finite correlation time. The difference between different situations will be only in the actual value of the diffusion coefficient D which is given by

$$D = \frac{1}{3} \int_0^\infty \langle \boldsymbol{v}(t) \cdot \boldsymbol{v}(0) \rangle dt, \tag{84}$$

see Eq. (71) [we assumed $\langle \boldsymbol{v} \rangle = 0$]. To apply the result to the Brownian motion we need to verify that $\boldsymbol{v}(t)$ has a finite correlation time τ_{cor} and find $\langle \boldsymbol{v}(t) \cdot \boldsymbol{v}(0) \rangle$. We already saw in the previous subsection that initial fluctuations of velocity decay within a characteristic time τ so that $\tau_{cor} \sim \tau$ so let us consider $\langle v_i(t)v_j(0) \rangle$. Using Eq. (73) one finds that the correlation function $\langle v_i(t)v_j(0) \rangle$ obeys

$$\frac{d}{dt}\langle v_i(t)v_j(0) \rangle = -\frac{\langle v_i(t)v_j(0) \rangle}{\tau} + \frac{\langle f_i(t)v_j(0) \rangle}{M}. \tag{85}$$

We note that due to causality $\boldsymbol{v}(0)$ is determined by $\boldsymbol{f}$ at negative times. Since $\boldsymbol{f}(t)$ is independent of $\boldsymbol{f}$ at negative times for $t \gg \tau_{cor}$, one concludes that $\boldsymbol{f}(t)$ and $\boldsymbol{v}(0)$ are independent random variables at $t \gg \tau_{cor}$. It follows that the average of the product is the product of averages or

$$\langle f_i(t)v_j(0) \rangle \approx \langle f_i(t) \rangle \langle v_j(0) \rangle = 0, \quad t \gg \tau_{cor}. \tag{86}$$

We conclude that

$$\frac{d}{dt}\langle v_i(t)v_j(0) \rangle \approx -\frac{\langle v_i(t)v_j(0) \rangle}{\tau}, \quad t \gg \tau_{cor}. \tag{87}$$

Next we note from the integral representation (79) of $\boldsymbol{v}(t)$ that the characteristic time of variations of $\boldsymbol{v}(t)$ is τ, so that at $t \ll \tau$ one has $\boldsymbol{v}(t) \approx \boldsymbol{v}(0)$ and thus $\langle v_i(t)v_j(0) \rangle \approx \langle v_i(0)v_j(0) \rangle$. As a result we can neglect times of order $\tau_{cor} \ll \tau$ in the evolution of $\langle v_i(t)v_j(0) \rangle$ and use

$$\frac{d}{dt}\langle v_i(t)v_j(0) \rangle \approx -\frac{\langle v_i(t)v_j(0) \rangle}{\tau}, \tag{88}$$

at any $t > 0$. The above equation on the correlation function is an expression of the Onsager principle, see below. We have

$$\langle v_i(t)v_j(0) \rangle = e^{-t/\tau}\langle v_i(0)v_j(0) \rangle = \frac{\delta_{ij}kT \exp[-t/\tau]}{M}. \tag{89}$$

Note that the friction coefficient determines the decay of the pair correlation function in time. Using Eq. (87) and integrating $\langle v_i(t)v_j(0)\rangle$ over time, we obtain the Einstein relation for the diffusion coefficient:

$$D = \frac{kT\tau}{M}.\tag{90}$$

The use of the expression (53) for τ produces the Einstein-Stokes relation that connects the coefficient of particle diffusion in a fluid and the fluid viscosity

$$D = \frac{kT}{6\pi\eta a}.\tag{91}$$

The above relation is useful for estimating the diffusion coefficient in a fluid with known viscosity, for example water. Note that, interestingly, D is independent of the particle mass: a particle with a different mass but the same size would have the same diffusion coefficient.

H. Effective white noise description

We saw in subsection IV E that as far as the statistics at large times is concerned one can substitute the original noise by the white noise with the same integral of dispersion. The same thing can be done in the calculations above. Without changing any of the answers one could substitute the original force in the Langevin equation (73) by any other force $\tilde{\boldsymbol{f}}$ having correlation time much smaller than τ, and obeying $\langle\tilde{\boldsymbol{f}}\rangle = 0$ and

$$\int\langle\tilde{f}_i(t)\tilde{f}_j(0)\rangle dt = \int\langle f_i(t)f_j(0)\rangle dt = \frac{2\delta_{ij}MkT}{\tau},\tag{92}$$

where we used Eq. (80). In other words, different types of microscopic (fluid) dynamics may lead to the same macroscopic dynamics (dynamics of the Brownian particle), cf. our treatment of perturbed harmonic oscillator. To see the equivalence note that both processes lead to Gaussian distribution of the process $\boldsymbol{v}(t)$. As such $\boldsymbol{v}(t)$ is completely determined by its average (equal to zero) and pair correlation function $\langle v_i(0)v_j(t)\rangle$. Since these are also the same for the two processes, the equivalence follows.

A particularly convenient choice of $\tilde{\boldsymbol{f}}$ is a Gaussian random force with $\langle\tilde{\boldsymbol{f}}\rangle = 0$ and

$$\langle\tilde{f}_i(t)\tilde{f}_j(t')\rangle = 2\delta_{ij}\delta(t - t')\frac{MkT}{\tau}.\tag{93}$$

The above noise with zero time correlation is often referred to as "white noise". The reason for the name will become clear when we discuss the spectral decomposition of fluctuations. The equivalence of the original $\boldsymbol{f}$ to $\tilde{\boldsymbol{f}}$ above is really an approximation: the white noise approximation, corresponding to taking the limit of zero τ_{cor}/τ just gives the leading order answers in τ_{cor}/τ. For "real" force $\boldsymbol{f}$ there are corrections both to Gaussianity of $\boldsymbol{v}$ and to $\langle v_i(0)v_j(t)\rangle$, which are small in the parameter $\tau_{cor}/\tau \ll 1$.

Thus for the analysis of the Brownian motion we may use the effective dynamics

$$\frac{d\boldsymbol{v}}{dt} = -\frac{\boldsymbol{v}}{\tau} + \frac{\tilde{\boldsymbol{f}}}{M}\tag{94}$$

Often it is the above dynamics with the white noise forcing that is called Langevin equation. From now on we will mostly use the effective white noise description in Langevin equations and we will omit tildas with no ambiguity. Let us now show an alternative way to obtain the effective description of the Brownian motion provided by Eqs. (93)-(94).

I. The Onsager regression to equilibrium hypothesis and the Langevin equation

The Brownian particle equation of motion written in the form

$$\frac{d\boldsymbol{v}}{dt} = -\frac{\boldsymbol{v}}{\tau} + \frac{\boldsymbol{f}}{M},\tag{95}$$

is but another form of the original Newton equation of motion $M\dot{v}_i = F_i$. However, introducing the assumption that the force $\boldsymbol{f}$ has correlation time much smaller than τ we were able to construct a rather detailed description of the

motion, reducible to Eqs. (93)-(94). In this subsection we will use another assumption on Eq. (95) that will lead us to the same Eqs. (93)-(94).

We will employ the Onsager regression to equilibrium hypothesis, which is not really a hypothesis as it seems to be true always. The hypothesis states that small fluctuations decay on average in exactly the same way as macroscopic deviations from equilibrium. To use the hypothesis we first need to understand what macroscopic deviations from equilibrium mean. For Brownian motion a macroscopic deviation from equilibrium is the situation where the value of the particle velocity is well above the typical value due to fluctuations, that is the thermal velocity $\sqrt{kT/M}$. For such values the dynamics of velocity is provided simply by non-random dynamics

$$\frac{d\boldsymbol{v}}{dt} = -\frac{\boldsymbol{v}}{\tau}. \tag{96}$$

Indeed, as we discussed in our derivation of Eq. (53), the equation above holds at large velocities. Formally, this can be seen by considering the equation on $\langle \boldsymbol{v} \rangle$ obtained by averaging Eq. (73):

$$\frac{d}{dt}\langle \boldsymbol{v} \rangle = -\frac{\langle \boldsymbol{v} \rangle}{\tau}. \tag{97}$$

The equation above reduces to Eq. (96) if initial velocity is much larger than $\sqrt{kT/M}$ (you are invited to show this in the homework). The above equation says that the fluctuating component of the force does not influence the decay of the average $\langle \boldsymbol{v} \rangle$ to its equilibrium value $\langle \boldsymbol{v} \rangle = 0$. This follows from the analysis made before when we mentioned that the non-random dynamics (53) is valid for large velocities. The reason is that fluctuating corrections have a certain fixed amplitude and they are negligible for velocities well above that amplitude. Qualitatively, this is natural - the velocity decay of particles in the fluid does looks deterministic corresponding to ordinary example of friction. Next, to express the Onsager hypothesis quantitatively we need to make a digression on the definition of correlation functions in equilibrium.

J. Digression: correlation functions in equilibrium

Let us consider two dynamical variables: functions $F_1(t) = F_1[\boldsymbol{p}(t), \boldsymbol{q}(t)]$ and $F_2(t) = F_2[\boldsymbol{p}(t), \boldsymbol{q}(t)]$ of the phase space variables of the system. We assume that the system is in equilibrium, say in the canonical ensemble with the temperature of reservoir T, and it is characterized by the corresponding equilibrium distribution $P_{eq}(\boldsymbol{p}, \boldsymbol{q})$ in the phase space. Now, even if $F_i(t)$ are macroscopic with their time averages given by the appropriate ensemble averages $\langle F_i \rangle$, still their value is not precisely a constant, rather it varies in time being only *on average* equal to the $\langle F_i \rangle$. We say that the variables F_i *fluctuate* near the average. For example, if $E(t)$ is the energy of a macroscopic subsystem with volume V_{sub} of a large closed system with energy E and volume $V \gg V_{sub}$, then on average $E(t) = EV_{sub}/V$, while at any given time $E(t) \neq EV_{sub}/V$ generally.

Below without any loss we will assume $\langle F_i \rangle = 0$ which can always by achieved by passing to $\tilde{F}_i(t) = F_i[\boldsymbol{p}(t), \boldsymbol{q}(t)] - \langle F_i \rangle$. Now for each system in the ensemble one has a particular time history of $F_i(t)$ and knowing the history of say $F_1(t)$ changes the probability of observing a particular time history of $F_2(t)$. A simple measure of correlations in fluctuations of F_i is the correlation function

$$\langle F_1(t)F_2(0) \rangle \equiv \int d\boldsymbol{p}_0 d\boldsymbol{q}_0 P_{eq}(\boldsymbol{p}_0, \boldsymbol{q}_0) F_1[\boldsymbol{p}(t|\boldsymbol{p}_0, \boldsymbol{q}_0), \boldsymbol{q}(t|\boldsymbol{p}_0, \boldsymbol{q}_0)] F_2[\boldsymbol{p}_0, \boldsymbol{q}_0], \tag{98}$$

where $\boldsymbol{p}(t|\boldsymbol{p}_0, \boldsymbol{q}_0)$, $\boldsymbol{q}(t|\boldsymbol{p}_0, \boldsymbol{q}_0)$ are the functions that give the time t momenta and coordinates of the particles given that at $t = 0$ they are given by $\boldsymbol{p}_0$ and $\boldsymbol{q}_0$ respectively. These functions, at least in principle, can be determined by solving the Hamilton equations of motion of the system

$$\frac{\partial \boldsymbol{p}(t|\boldsymbol{p}_0, \boldsymbol{q}_0)}{\partial t} = -\frac{\partial H}{\partial \boldsymbol{q}}, \quad \frac{\partial \boldsymbol{q}(t|\boldsymbol{p}_0, \boldsymbol{q}_0)}{\partial t} = \frac{\partial H}{\partial \boldsymbol{p}}, \quad \boldsymbol{p}(0|\boldsymbol{p}_0, \boldsymbol{q}_0) = \boldsymbol{p}_0, \quad \boldsymbol{q}(0|\boldsymbol{p}_0, \boldsymbol{q}_0) = \boldsymbol{q}_0. \tag{99}$$

Operationally, what the above definition of the correlation function does is as follows. At $t = 0$ each system in the ensemble has a definite value of momenta $\boldsymbol{p}_0$ and coordinates $\boldsymbol{q}_0$. These determine completely the momenta and coordinates at later times. In particular, for each system in the ensemble the initial values $\boldsymbol{p}_0$ and $\boldsymbol{q}_0$ determine $F_2(0) = F_2[\boldsymbol{p}_0, \boldsymbol{q}_0]$ and $F_1(t) = F_1[\boldsymbol{p}(t|\boldsymbol{p}_0, \boldsymbol{q}_0), \boldsymbol{q}(t|\boldsymbol{p}_0, \boldsymbol{q}_0)]$. Taking now the product of the last two and averaging over different $\boldsymbol{p}_0$, $\boldsymbol{q}_0$ with their appropriate probability weights produces the correlation function $\langle F_1(t)F_2(0) \rangle$. Clearly, $\langle F_1(t)F_2(0) \rangle$ is a measure of correlations in temporal fluctuations of $F_i(t)$. Because equilibrium is a statistically stationary state the choice of the initial moment of time is not essential, $\langle F_1(t)F_2(0) \rangle = \langle F_1(t + t_0)F_2(t_0) \rangle$ for any t_0.

The latter equality can be seen directly by using $\boldsymbol{p}(t|\boldsymbol{p}_0, \boldsymbol{q}_0) = \boldsymbol{p}(t + t_0|t_0, \boldsymbol{p}_0, \boldsymbol{q}_0)$ and $\boldsymbol{q}(t|\boldsymbol{p}_0, \boldsymbol{q}_0) = \boldsymbol{q}(t + t_0|t_0, \boldsymbol{p}_0, \boldsymbol{q}_0)$ with the appropriate definitions of $\boldsymbol{p}(t + t_0|t_0, \boldsymbol{p}_0, \boldsymbol{q}_0)$ and $\boldsymbol{q}(t + t_0|t_0, \boldsymbol{p}_0, \boldsymbol{q}_0)$

Let us now apply the definition above to the Brownian motion problem. The equilibrium system in this case is the composite system "fluid plus particle". The dynamical variables of this system are the fluid particles momenta and coordinates, $\boldsymbol{p}$ and $\boldsymbol{q}$ respectively, and the velocity $\boldsymbol{v}$ (equivalent to momentum) and position $\boldsymbol{x}$ of the Brownian particle. The equilibrium distribution function obeys the decomposition

$$P_{eq}(\boldsymbol{p}, \boldsymbol{q}, \boldsymbol{v}, \boldsymbol{x}) = P_M(\boldsymbol{v})\tilde{P}(\boldsymbol{p}, \boldsymbol{q}, \boldsymbol{x}), \tag{100}$$

where $P_M(\boldsymbol{v})$ is the Maxwell distribution at the system temperature T. Let us now consider the correlation function $\langle v_i(t)v_j(0)\rangle$ that describes the correlations in the fluctuations of the Brownian particle velocity. These fluctuations can be easily illustrated for a gas: though on average $\boldsymbol{v} = 0$, still the bumps exerted on the particle by the gas particles are almost always not in the precise balance and particle velocity gets increased in some directions, then decreased back and so further. Now applying the general definition of the correlation function (98) to two functions $F_1[\boldsymbol{p}(t), \boldsymbol{q}(t), \boldsymbol{v}(t), \boldsymbol{x}(t)] \equiv v_i(t)$ and $F_2[\boldsymbol{p}(t), \boldsymbol{q}(t), \boldsymbol{v}(t), \boldsymbol{x}(t)] \equiv v_j(t)$ we get

$$\langle v_i(t)v_j(0)\rangle = \int d\boldsymbol{p}_0 d\boldsymbol{q}_0 d\boldsymbol{v}_0 d\boldsymbol{x}_0 P_M(\boldsymbol{v}_0)\tilde{P}(\boldsymbol{p}_0, \boldsymbol{q}_0, \boldsymbol{x}_0)v_i(t|\boldsymbol{p}_0, \boldsymbol{q}_0, \boldsymbol{v}_0, \boldsymbol{x}_0)v_{0j} = \int d\boldsymbol{v}_0 P_M(\boldsymbol{v}_0)H_i(t|\boldsymbol{v}_0)v_{0j}, \tag{101}$$

where we used Eq. (100) and defined the conditional average

$$H_i(t|\boldsymbol{v}_0) \equiv \int d\boldsymbol{p}_0 d\boldsymbol{q}_0 d\boldsymbol{x}_0 \tilde{P}(\boldsymbol{p}_0, \boldsymbol{q}_0, \boldsymbol{x}_0)v_i(t|\boldsymbol{p}_0, \boldsymbol{q}_0, \boldsymbol{v}_0, \boldsymbol{x}_0). \tag{102}$$

We are now ready to formulate the Onsager hypothesis.

K. The Onsager hypothesis

From the fact that Brownian particle obeys at large velocities the simple friction equation (96) it follows that

$$\frac{dH_i(t|\boldsymbol{v}_0)}{dt} = -\frac{H_i(t|\boldsymbol{v}_0)}{\tau}, \tag{103}$$

at sufficiently large v_0 and not too large t. Now, equation (96) describes the system (fluid plus particle) relaxation to equilibrium after the creation of an initial macroscopic deviation in the particle velocity. On the other hand, the initial fluctuation of velocity could arise just "by itself" because the system fluctuates even if in equilibrium. The fluctuation does not mean $\langle \boldsymbol{v}(t = 0)\rangle \neq 0$, it only means that $\boldsymbol{v}(t = 0)$ is generally non-zero for most of the systems in the ensemble. Still if say initially $v_x(t = 0)$ is positive one expects that this positive value would be forgotten in time, it would decay in some sense just like $\langle \boldsymbol{v} \rangle$. The Onsager hypothesis quantifies this expectation. The hypothesis extends Eq. (103) to arbitrary v_0 and t. This extension is rather natural because $H_i(t|\boldsymbol{v}_0)$ is quantity which is already averaged over the states of the fluid and thus the equation on $H_i(t|\boldsymbol{v}_0)$ in contrast to the equation on $\boldsymbol{v}$ should not involve any corrections due to fluctuations.

By Eq. (101) Eq. (103) implies that the correlation function $\langle v_i(t)v_j(0)\rangle$ satisfies an equation of exactly the same form as Eq. (97), namely:

$$\frac{d}{dt}\langle v_i(t)v_j(0)\rangle = -\frac{\langle v_i(t)v_j(0)\rangle}{\tau}. \tag{104}$$

While the above equation could be derived from the Langevin equation (73), here it does not involve an explicit consideration of the decomposition of the forces employed in (73). One can say that the Onsager hypothesis postulates Eq. (104) instead of postulating that the force in the Langevin equation has correlation time much smaller than τ which is the assumption we used before. Obviously, Eq. (104) implies

$$\langle v_i(t)v_j(0)\rangle = e^{-|t|/\tau}\langle v_i(0)v_j(0)\rangle = e^{-|t|/\tau}\delta_{ij}\frac{kT}{M}. \tag{105}$$

where we used the equipartition theorem. Now, in contrast to our derivation of the above result from the Langevin equation, here the above equation becomes the starting point of the analysis of Brownian motion. If one starts with the above equation and introduces the force $\boldsymbol{f}$ by Eq. (95) then it holds that $\boldsymbol{f}$ has the same statistics as the white noise $\tilde{\boldsymbol{f}}$ introduced before. This can be verified directly with the help of Eq. (75) or by another method that we pass to consider.

L.   Spectral decomposition of fluctuations

Definition of the spectral decomposition and the spectrum.... The noise is called "white" because it contains all frequencies just like white color contains all colors...

M.   Relaxation to equilibrium and Newton's law of cooling

As an introduction to the theory of thermodynamic fluctuations considered in the next Section, let us consider the evolution of $\langle v^2(t) \rangle$. We have

$$\frac{d}{dt}\langle v^2(t)\rangle = 2\langle \boldsymbol{v} \cdot \frac{d\boldsymbol{v}}{dt}\rangle = -\frac{2\langle v^2\rangle}{\tau} + \frac{2\langle \boldsymbol{v}(t) \cdot \boldsymbol{f}(t)\rangle}{M}, \tag{106}$$

where we used Langevin equation (73). To find the average appearing in the last term above we use the explicit expression (79) for $\boldsymbol{v}(t)$. We find

$$\langle \boldsymbol{v}(t) \cdot \boldsymbol{f}(t)\rangle = \langle \boldsymbol{v}(0) \cdot \boldsymbol{f}(t)\rangle e^{-t/\tau} + \frac{1}{M}\int_0^t e^{-(t-t')/\tau}\langle \boldsymbol{f}(t') \cdot \boldsymbol{f}(t)\rangle dt'. \tag{107}$$

The average $\langle \boldsymbol{v}(0) \cdot \boldsymbol{f}(t)\rangle$ already occurred in our treatment of $\langle v_i(t)v_j(0)\rangle$ where it was shown small at $t \gg \tau_{cor}$. On the other hand for the last term above, using that the correlation function in the integrand decays fast at $t-t' \gg \tau_{cor}$, where $\tau_{cor} \ll \tau$, we obtain

$$\frac{1}{M}\int_0^t e^{-(t-t')/\tau}\langle \boldsymbol{f}(t') \cdot \boldsymbol{f}(t)\rangle dt' \approx \frac{1}{M}\int_{-\infty}^t \langle \boldsymbol{f}(t') \cdot \boldsymbol{f}(t)\rangle dt' = \frac{3kT}{\tau}, \tag{108}$$

where we used the FDT in the form of Eq. (81). It follows that we may rewrite Eq. (107) as

$$\frac{d}{dt}\langle v^2(t)\rangle = -\frac{2\left[\langle v^2\rangle - 3kT/M\right]}{\tau}. \tag{109}$$

The above equation describes exponential relaxation of $\langle v^2(t)\rangle$ to its equilibrium value $3kT/M$ given by the equipartition theorem. It can be given a suggestive form if we formally introduce the temperature of the Brownian particle $T(t)$ by reverting the equipartition theorem (cf. our definition of temperature for an ergodic system given by Eq. (31)

$$T(t) \equiv \frac{M\langle v^2(t)\rangle}{3k}. \tag{110}$$

Then, designating for the purposes of this subsection the fluid temperature by T_e, with subscript standing for "environment", we find that $T(t)$ obeys

$$\frac{dT}{dt} = -\frac{T - T_e}{\tau_{rel}}, \quad \tau_{rel} \equiv \frac{\tau}{2}. \tag{111}$$

It follows that the evolution of $\langle v^2(t)\rangle$ can be seen as a relaxation of the "temperature" of Brownian particle to the temperature of the environment T_e (here the environment is nothing but the ambient fluid).

The above law, though it was obtained in a particular case and somewhat artificially, is in fact a general law that was discovered by Newton. Newton's Law of Cooling states that the rate of change of the temperature of an object is proportional to the difference between its own temperature and the ambient temperature (i.e. the temperature of its surroundings).

In particular the law applies to the following situation. Consider a subsystem of a large system at equilibrium at some temperature. Assume that the subsystem, though it is much smaller than the whole system, is sufficiently large so that we can speak of its temperature. Now if for some reason the temperature of the subsystem T_{sub} deviates from the temperature of the whole system T_e, then a relaxation process starts, and it also obeys the Newton law

$$\frac{dT_{sub}}{dt} = -\frac{T_{sub} - T_e}{\tau_{rel}}, \tag{112}$$

with some τ_{rel}. Again one can neglect here the minute variations of the temperature of the whole system and consider it constant throughout the process. Now a possible source of the deviation of T_{sub} from T_e is just natural fluctuations in the system: all thermodynamic variables (and T_{sub} is a one) fluctuate in equilibrium and only on average they are equal to their values provided by thermodynamics. This brings us to our next subject - the theory of thermodynamics fluctuations that will be discussed after the following exercise using the theory of Brownian motion.

N.   An exercise: dumbbell model of a polymer

Consider a simple dumbbell model of a polymer that consists of two identical spherical particles with radius a connected by a spring with spring constant k. The dumbbell is immersed in a fluid. One can assume that random components of the force acting on each spherical particle are independent and given by a white noise. In all parts of the problem one can neglect the hard spheres interaction of the particles. The fluid temperature T and mass M are known.

A. Use the equipartition theorem to obtain the equilibrium average value of the relative coordinate between the particles.

B. Write down the Langevin equations of motion on the center of mass and the relative coordinates of the particles. Which one of them performs diffusion and which does not? What is the diffusion coefficient and how is it related to the diffusion coefficient of the single sphere? Using the expression for relaxation time provided in class determine if the diffusion coefficient depends on the mass of the particles.

C. Derive the spectrum of fluctuations of the relative coordinate and determine the corresponding correlation function as a function of time. Is the result of A reproduced?

D. Derive the correlation function of the relative velocity. Can you see from this expression that relative coordinate does not perform diffusion at large times?

E. What is the equilibrium distribution function of the coordinates and velocities?

Solution.

A. The Hamiltonian of the system is

$$H = \frac{p_1^2}{2M} + \frac{p_2^2}{2M} + \frac{k(\boldsymbol{x}_2 - \boldsymbol{x}_1)^2}{2}. \tag{113}$$

By the equipartition theorem each degree of freedom above gets energy $kT/2$ so that

$$\langle |\boldsymbol{x}_2 - \boldsymbol{x}_1|^2 \rangle = \frac{3k_B T}{k}. \tag{114}$$

B. The Langevin equations of motion on each particle are

$$\frac{d\boldsymbol{v}_i}{dt} = -\frac{\boldsymbol{v}_i}{\tau} - \frac{1}{M}\frac{\partial}{\partial \boldsymbol{x}_i}\frac{k(\boldsymbol{x}_2 - \boldsymbol{x}_1)^2}{2} + \frac{\boldsymbol{f}_i}{M}, \tag{115}$$

where $\boldsymbol{f}_i$ are independent noises with pair correlation function

$$\langle f_{1i}(t)f_{1j}(t') \rangle = 2\delta_{ij}\delta(t - t')\frac{Mk_B T}{\tau}, \tag{116}$$

and similar expression for $\boldsymbol{f}_2$. The center of mass velocity $\boldsymbol{V} = [\boldsymbol{v}_1 + \boldsymbol{v}_2]/2$ and coordinate $\boldsymbol{X} = [\boldsymbol{x}_1 + \boldsymbol{x}_2]/2$ satisfy

$$\frac{d\boldsymbol{V}}{dt} = -\frac{\boldsymbol{V}}{\tau} + \frac{\boldsymbol{g}}{M}, \quad \frac{d\boldsymbol{X}}{dt} = \boldsymbol{V}, \quad \boldsymbol{g} \equiv \frac{\boldsymbol{f}_1 + \boldsymbol{f}_2}{2}. \tag{117}$$

The relative velocity $\boldsymbol{v} = \boldsymbol{v}_2 - \boldsymbol{v}_1$ and coordinate $\boldsymbol{x} = \boldsymbol{x}_2 - \boldsymbol{x}_1$ obey

$$\frac{d\boldsymbol{v}}{dt} = -\frac{\boldsymbol{v}}{\tau} - \frac{2k\boldsymbol{x}}{M} + \frac{\boldsymbol{h}}{M}, \quad \frac{d\boldsymbol{x}}{dt} = \boldsymbol{v}, \quad \boldsymbol{h} \equiv \boldsymbol{f}_2 - \boldsymbol{f}_1. \tag{118}$$

Note that the noises $\boldsymbol{g}$ and $\boldsymbol{h}$ are independent $\langle g_i h_j \rangle \propto \langle f_{1i}f_{1j} \rangle - \langle f_{2i}f_{2j} \rangle = 0$. It follows that the center of mass performs diffusion just like in the analysis in class, with the diffusion coefficient $D = k_B T\tau/2M$, that is one half the diffusion coefficient of the single sphere. The latter formula can be seen by noting that $\langle g_i(t)g_j(t') \rangle = \langle f_{1i}(t)f_{2j}(t') \rangle/2$ which is equivalent to the renormalizing the temperature by factor of two. Note that the result is independent of the spring constant: center of mass motion does not know about the interactions. In particular the same diffusion coefficient would hold for particles that don't interact at all as follows from

$$\langle X^2(t) \rangle = \frac{1}{4}\left[\langle x_1^2(t) \rangle + \langle x_2^2(t) \rangle + 2\langle \boldsymbol{x}_1(t) \cdot \boldsymbol{x}_2(t) \rangle \right] \approx \frac{\langle x_1^2(t) \rangle + \langle x_2^2(t) \rangle}{4} = \frac{D_s t}{2}, \tag{119}$$

where D_s is the single particle diffusion coefficient, $\langle x_i^2(t) \rangle \approx D_s t$. Above the approximation holds at large times and we used that $\boldsymbol{x}_i$ are independent for non-interacting particles so that $\langle \boldsymbol{x}_1(t) \cdot \boldsymbol{x}_2(t) \rangle = \langle \boldsymbol{x}_1(t) \rangle \cdot \langle \boldsymbol{x}_2(t) \rangle = const$ by conservation of $\langle \boldsymbol{x}_1(t) \rangle$. Also note that the center of mass diffusion coefficient is equal to the diffusion coefficient of

the particle with twice the mass of each particle. Finally, the diffusion coefficient is independent of the mass of the particles (cf. the Einstein-Stokes relation), since $\tau/M = 1/6\pi\eta a$ is independent of it.

C. Passing to Eq. (118) we observe that it can be written as

$$\frac{d^2\boldsymbol{x}}{dt^2} + \frac{1}{\tau}\frac{d\boldsymbol{x}}{dt} + \frac{2k\boldsymbol{x}}{M} = \frac{\boldsymbol{h}}{M}. \tag{120}$$

Performing Fourier transform of the above equation we find that in the steady state (where homogeneous part of the solution of the above equation can be dropped) we have

$$\left[-\omega^2 - \frac{i\omega}{\tau} + \frac{2k}{M}\right]\boldsymbol{x}(\omega) = \frac{h(\omega)}{M}. \tag{121}$$

It follows that the spectrum of $\boldsymbol{x}$ defined by

$$\langle x_i(\omega)x_j(\omega')\rangle = (2\pi)E_{ij}(\omega)\delta(\omega+\omega'), \tag{122}$$

obeys

$$\left|-\omega^2 - \frac{i\omega}{\tau} + \frac{2k}{M}\right|^2 E_{ij}(\omega) = \frac{E_{ij}^h(\omega)}{M^2} \tag{123}$$

where $E_{ij}^h(\omega)$ is the spectrum of $\boldsymbol{h}$ that obeys

$$E_{ij}^h(\omega) = \int \langle h_i(t)h_j(0)\rangle e^{i\omega t}dt = 2\int \langle f_{1i}(t)f_{1j}(0)\rangle e^{i\omega t}dt = \frac{4Mk_BT\delta_{ij}}{\tau}. \tag{124}$$

For the pair-correlation function of $\boldsymbol{x}$ we find

$$\langle x_i(t)x_j(0)\rangle = \int_{-\infty}^{\infty} E_{ij}(\omega)e^{-i\omega t}\frac{d\omega}{2\pi} = \frac{4k_BT\delta_{ij}}{M\tau}\int_{-\infty}^{\infty}\frac{e^{-i\omega t}}{|-\omega^2 - i\omega/\tau + 2k/M|^2}\frac{d\omega}{2\pi}$$

$$= \frac{2k_BT\delta_{ij}}{M}\int_{i\epsilon-\infty}^{i\epsilon+\infty}\frac{d\omega}{2\pi i}\frac{\exp[i\omega t]}{\omega}\left[\frac{1}{\omega^2 - i\omega/\tau - 2k/M} - \frac{1}{\omega^2 + i\omega/\tau - 2k/M}\right], \tag{125}$$

where in the last line we used that the integral is an even function of t which can be easily seen from the expressions in the first line. We also raised the integration line in the complex plane by an infinitesimal amount for convenience in the following calculations. We note that we can close the contour in the upper half-plane and by Cauchy theorem transform the integral into the contribution from the poles of the integrand. Noting that the poles that come from the last term are always in the lower half-plane we obtain

$$\langle x_i(t)x_j(0)\rangle = \frac{2k_BT\delta_{ij}}{M}\int_{i\epsilon-\infty}^{i\epsilon+\infty}\frac{d\omega}{2\pi i}\frac{\exp[i\omega t]}{\omega}\frac{1}{\omega^2 - i\omega/\tau - 2k/M}. \tag{126}$$

Note that by differentiating $\exp[i\omega t]$ in the integral one has

$$\left[\frac{d^2}{dt^2} + \frac{1}{\tau}\frac{d}{dt} + \frac{2k}{M}\right]\langle x_i(t)x_j(0)\rangle = -\frac{2k_BT\delta_{ij}}{M}\int_{i\epsilon-\infty}^{i\epsilon+\infty}\frac{d\omega}{2\pi i}\frac{\exp[i\omega t]}{\omega}, \tag{127}$$

where the first term in brackets acts on the correlation function as an operator. At any $t > 0$ one can close the contour to see that the integral in the RHS of the above equation is zero. This is not surprising: by Eq. (120) we have

$$\left[\frac{d^2}{dt^2} + \frac{1}{\tau}\frac{d}{dt} + \frac{2k}{M}\right]\langle x_i(t)x_j(0)\rangle = \frac{\langle h_i(t)x_j(0)\rangle}{M}, \tag{128}$$

where the last term vanishes at $t > 0$ because $h(t)$ is δ−correlated in time, while $\boldsymbol{x}(0)$ depends only on $\boldsymbol{h}(t)$ at $t \leq 0$ leading to $\langle h_i(t)x_j(0)\rangle = \langle h_i(t)\rangle\langle x_j(0)\rangle = 0$. Returning to Eq. (126) and introducing

$$\omega_1 = \frac{i}{2\tau} + \sqrt{-\frac{1}{4\tau^2} + \frac{2k}{M}}, \quad \omega_1 = \frac{i}{2\tau} - \sqrt{-\frac{1}{4\tau^2} + \frac{2k}{M}}, \tag{129}$$

we have

$$\langle x_i(t)x_j(0)\rangle = \frac{2k_BT\delta_{ij}}{M} \int_{i\epsilon-\infty}^{i\epsilon+\infty} \frac{d\omega}{2\pi i} \frac{\exp[i\omega t]}{\omega(\omega_1-\omega_2)} \left[\frac{1}{\omega-\omega_1} - \frac{1}{\omega-\omega_2}\right]. \tag{130}$$

The above integral is readily expressed in terms of the contributions of two poles as

$$\langle x_i(t)x_j(0)\rangle = \frac{2k_BT\delta_{ij}}{M(\omega_1-\omega_2)} \left[\frac{\exp[i\omega_1 t]}{\omega_1} - \frac{\exp[i\omega_2 t]}{\omega_2}\right]. \tag{131}$$

which is our final answer. The above expression must be real which can be checked by considering separately the cases where the square root in Eq. (129) is real and purely imaginary. At $t=0$ we have

$$\langle x_i(t)x_j(0)\rangle = -\frac{2k_BT\delta_{ij}}{M\omega_1\omega_2} = \frac{k_BT\delta_{ij}}{k}, \tag{132}$$

which reproduces Eq. (114) after taking the trace. We also have from Eq. (131) that

$$\frac{d}{dt}\langle x_i(t)x_j(0)\rangle|_{t=0} = \frac{2k_BT\delta_{ij}}{M(\omega_1-\omega_2)} \left[i\exp[i\omega_1 t] - i\exp[i\omega_2 t]\right]|_{t=0} = 0. \tag{133}$$

Observing that $d/dt\langle x_i(t)x_j(0)\rangle|_{t=0}$ is nothing but $\langle v_i(0)x_j(0)\rangle$ we see that the above agrees with the result obtained from the equilibrium statistical mechanics dictating $\langle v_i(0)x_j(0)\rangle = 0$. Note that Eq. (128), together with the last two equations considered as input from equilibrium statistical mechanics, could be used as an alternative way to determine $\langle x_i(t)x_j(0)\rangle$. This would necessarily lead to Eq. (131) showing the consistency of the whole calculation. In particular, $\langle x_i(t)x_j(0)\rangle$ considered as a function of t describes an unforced damped harmonic oscillator with zero initial velocity and finite deviation from zero. Finally, this is nothing but an expression of the Onsager principle, stating that $\langle x_i(t)x_j(0)\rangle$ should relax in the same way as $x_i(t)$ in the absence of the random force.

D. For the correlation function of the relative velocity in the steady state we have

$$\langle v_i(t_1)v_j(t_2)\rangle = \frac{d}{dt_1}\frac{d}{dt_2}\langle x_i(t_1)x_j(t_2)\rangle = -\frac{d^2}{dt_1^2}\langle x_i(t_1)x_j(t_2)\rangle, \tag{134}$$

where we used that in the steady state $\langle x_i(t_1)x_j(t_2)\rangle$ is a function of t_2-t_1 only. Using the expression for $\langle x_i(t)x_j(0)\rangle$ we obtain

$$\langle v_i(t)v_j(0)\rangle = -\frac{d^2}{dt^2}\langle x_i(t)x_j(0)\rangle = \frac{2k_BT\delta_{ij}}{M(\omega_1-\omega_2)} \left[\omega_1 e^{i\omega_1 t} - \omega_2 e^{i\omega_2 t}\right] = \frac{2k_BT\delta_{ij}}{iM(\omega_1-\omega_2)} \frac{\partial}{\partial t} \left[e^{i\omega_1 t} - e^{i\omega_2 t}\right].$$

The above way of determining the correlation function of the process derivative from the correlation function of the process itself holds for stationary processes generally. Again one can check that the expression above is real. We observe that the diffusion coefficient D which is proportional to $\int_0^\infty \langle \boldsymbol{v}(t)\cdot\boldsymbol{v}(0)\rangle dt$ vanishes identically for the velocity correlation function above. The correlation function is not sign-definite in this case: it changes sign which signifies that there are anti-correlations in velocity. Such anti-correlations are natural consequences of the spring that after a while causes the reversal in the original direction of motion of the oscillator. Note that vanishing of D is necessary for consistency: otherwise the fluctuations of $\boldsymbol{x}$ would have to grow diffusively at large times.

E. The equations on all quantities, both coordinates and velocities, belong to the general type of equations of the type

$$\frac{d\boldsymbol{b}}{dt} = \hat{M}\boldsymbol{b} + \boldsymbol{f}, \tag{135}$$

where $\boldsymbol{b}(t)$ is some vector, $\hat{M}$ is a constant matrix and $\boldsymbol{f}$ is a vector of random forces assumed Gaussian. The above equation leads to the following expression for $\boldsymbol{b}$ in the steady state (assuming that the latter exists):

$$\boldsymbol{b}(t) = \int_{-\infty}^{t} \exp[(t-t')\hat{M}]\boldsymbol{f}(t')dt'. \tag{136}$$

It follows from the above expression that $\boldsymbol{b}(t)$ is a linear functional of a Gaussian process and hence it is also Gaussian. We conclude that the statistics of $\boldsymbol{x}$, $\boldsymbol{X}$, $\boldsymbol{v}$ and $\boldsymbol{V}$ are all Gaussian and thus determined uniquely by the averages and the dispersions. These can readily found using equipartition theorem and the description of diffusion that was provided in class. Note that though for $\boldsymbol{X}$ there is no steady state still Gaussianity applies as was shown when the diffusion was discussed.

V. THEORY OF THERMODYNAMIC FLUCTUATIONS AND LINEAR LANGEVIN EQUATIONS FOR SLOW VARIABLES

It turns out that the Brownian motion considered in the previous Section is a prototype problem for the general theory of thermodynamic fluctuations near equilibrium. Let us start with an example.

A. Brownian motion of other variables

Consider a first-order isomerization reaction between two species called A and B. We denote the number of molecules of each species by the same letters. Note that both, A and B are macroscopic variables of the order of Avogadro number. The basic rate equations are

$$\frac{dA}{dt} = -k_1 A + k_2 B, \quad \frac{dB}{dt} = -k_2 B + k_1 A, \tag{137}$$

The coefficients above are such that to ensure the conservation of the total number of molecules $A + B$. The equations have equilibrium solution A_{eq}, B_{eq} satisfying the equilibrium condition $k_1 A_{eq} = k_2 B_{eq}$. Using the conservation of $A + B$ we may substitute two equations by one. Introducing the deviation C from equilibrium, $C = A - A_{eq} = B - B_{eq}$, we find

$$\frac{dC}{dt} = -(k_1 + k_2)C. \tag{138}$$

Thus the macroscopic deviation from equilibrium decays exponentially. Now if the system reaches thermal equilibrium then by the general FDT there are fluctuations and in particular $\langle C^2 \rangle_{eq}$ is of the order of Avogadro number and cannot vanish. The Onsager hypothesis leads to the following correlation function of fluctuations

$$\langle C(t)C(t') \rangle = \langle C^2 \rangle_{eq} e^{-(k_1+k_2)|t-t'|}. \tag{139}$$

Obviously, Eq. (138) cannot lead to the above formula. As in our discussion of the Onsager hypothesis for Brownian motion to account for fluctuations a random force or noise term should be added to the basic kinetic equation (138):

$$\frac{dC}{dt} = -(k_1 + k_2)C + \delta F(t). \tag{140}$$

The force $\delta F(t)$ describes the molecular source of fluctuations. To have the correct equilibrium behavior we must impose the FDT in the form

$$\langle \delta F(t)\delta F(t') \rangle = 2(k_1 + k_2)\langle C^2 \rangle_{eq}\delta(t - t'). \tag{141}$$

Thus observation of particle number fluctuations over a very long time can be used to find a rate constant. Let us now generalize the above example.

B. General equation for slow variables near equilibrium

Both the Brownian motion and the example above are particular cases of a very general dynamics holding near equilibrium. This dynamics holds for slow or macroscopic variables. These variables are such that they change but a little at time-scales sufficient for the rest of the system to relax to what is called the state of "partial equilibrium". In the latter state the rest of the system can be characterized by a certain statistical ensemble which depends on the values of the slow variables as parameters. Let us designate the slow variables by x_i and assume that we already subtracted the average so that equilibrium values of x_i are zero. For example, components of velocity of Brownian particle are slow variables. The variables x_i have a characteristic time τ during which they relax to their equilibrium (zero) values if excited initially. Now if τ is much larger than the relaxation time of the rest of the system then the latter would be all the time in a "quasiequilibrium" state determined by the instantaneous values of $x_i(t)$. In other words, the rest of the system, "fast variables" will be enslaved by slow variables, cf. our discussion in the first Section. If we now write equations of motion for slow variables then they are closed - the impact of fast variables on the slow ones is determined only by the values of the slow variables which enslaved the fast ones. As a result, the equation of motion on x_i takes the form

$$\frac{dx_i}{dt} = R_i(x_1, x_2, ..., x_n), \tag{142}$$

where the function R_i is determined by the partial equilibrium state of the fast variables. If we consider small deviations from equilibrium, then we can expand R_i in Taylor series. Keeping only the lowest order term we find

$$\frac{dx_i}{dt} = -\lambda_{ik}x_k, \tag{143}$$

where the summation convention over repeated indices is assumed. To explain the above notions, we consider again the example of Brownian motion.

C. The Onsager reciprocal relations

We have seen above that the relaxation of the slow variable $\boldsymbol{v}$ obeys the equation $\dot{v}_i = F_i(\boldsymbol{v})/M$, where the force $\boldsymbol{F}(\boldsymbol{v})$ in linear in a range of velocities far exceeding the characteristic thermal velocity. The equation on $\boldsymbol{v}$ gets closed because the state of the fast degrees of freedom of the system - the degrees of freedom of the fluid - is determined uniquely by $\boldsymbol{v}$, see Eqs. (**??**). As a result the force which the fast variables exert on the slow variable is determined by the latter uniquely, leading to an equation of the type $\dot{v}_i = F_i(\boldsymbol{v})/M$.

Generally the theory of fluctuations of slow variables near equilibrium assumes the generalized force equation (142) where the "force" $R_i(x_1, x_2, .., x_n)$ obeys

$$R_i(x_1, x_2, .., x_n) \approx -\lambda_{ik}x_k, \quad |x_i| \ll x_0, \tag{144}$$

with $x_0 \gg \max\langle x_i^2 \rangle^{1/2}$. The above condition guarantees that equilibrium fluctuations all occur in the region of linear reaction of the system and it allows to employ the linear relaxation equations (143) in the range $\max\langle x_i^2 \rangle^{1/2} \ll |x_i| \ll x_0$. Let us stress that the latter equations are deterministic and hold for every realization of the relaxation process. We also stress that is assumed that x_i represent a *complete* set of slow variables, i. e. $x_i(t)$ characterize the relaxation process completely and no additional deviations from the equilibrium arises (to give a simple example: the relative coordinate in the dumbbell model of the polymer is not a complete set of slow variables as its excitation also leads to the excitation of the relative velocity).

Different time correlation functions $\varphi_{ij}(t) \equiv \langle x_i(t)x_j(0) \rangle$ obey special symmetry properties following from the time reversal symmetry of the microscopic dynamics. Since by the Onsager principle these functions satisfy

$$\frac{d\varphi_{ij}}{dt} = -\lambda_{ik}\varphi_{kj}, \tag{145}$$

then the coefficients λ_{ik} must obey a constraint ensuring that the correlation functions obtained via the equation above obey the required symmetry properties. Let us derive this constraint.

By the stationarity of the equilibrium state we have that $\langle x_i(t)x_j(0) \rangle = \langle x_i(0)x_j(-t) \rangle$ or $\varphi_{ij}(t) = \varphi_{ji}(-t)$. Formally this property could be seen by considering the pair correlation function of two dynamical variables $F_i(\boldsymbol{p}, \boldsymbol{q})$ as it was defined by Eq. (98), which we for convenience reproduce here

$$\langle F_1(t)F_2(0) \rangle \equiv \int d\boldsymbol{p}_0 d\boldsymbol{q}_0 P_{eq}(\boldsymbol{p}_0, \boldsymbol{q}_0) F_1[\boldsymbol{p}(t|\boldsymbol{p}_0, \boldsymbol{q}_0), \boldsymbol{q}(t|\boldsymbol{p}_0, \boldsymbol{q}_0)]F_2[\boldsymbol{p}_0, \boldsymbol{q}_0]. \tag{146}$$

Let us introduce new integration variables $\boldsymbol{p}' = \boldsymbol{p}(t|\boldsymbol{p}_0, \boldsymbol{q}_0)$ and $\boldsymbol{q}' = \boldsymbol{q}(t|\boldsymbol{p}_0, \boldsymbol{q}_0)$. Then because the Hamiltonian in the equations of motion has no explicit time dependence, one can write the inverse transformation as $\boldsymbol{p}_0 = \boldsymbol{p}(-t|\boldsymbol{p}', \boldsymbol{q}')$ and $\boldsymbol{q}_0 = \boldsymbol{q}(-t|\boldsymbol{p}', \boldsymbol{q}')$ which leads to

$$\langle F_1(t)F_2(0) \rangle = \int d\boldsymbol{p}' d\boldsymbol{q}' P_{eq}(\boldsymbol{p}', \boldsymbol{q}') F_1[\boldsymbol{p}', \boldsymbol{q}']F_2[\boldsymbol{p}(-t|\boldsymbol{p}', \boldsymbol{q}'), \boldsymbol{q}(-t|\boldsymbol{p}', \boldsymbol{q}')] = \langle F_1(0)F_2(-t) \rangle, \tag{147}$$

which is the desired relation. Above we used that the stationary probability weight is conserved along the dynamical trajectory, $P_{eq}(\boldsymbol{p}_0, \boldsymbol{q}_0)d\boldsymbol{p}_0 d\boldsymbol{q}_0 = P_{eq}(\boldsymbol{p}', \boldsymbol{q}')d\boldsymbol{p}' d\boldsymbol{q}'$. To derive the relation due to the time reversal symmetry, we make another change of variables in the integral in Eq. (146): we switch from $\boldsymbol{p}_0$ to $-\boldsymbol{p}_0$, leaving $\boldsymbol{q}$ intact. Noting that the time-reversal symmetry of mechanics implies

$$\boldsymbol{p}(t| - \boldsymbol{p}_0, \boldsymbol{q}_0) = -\boldsymbol{p}(-t|\boldsymbol{p}_0, \boldsymbol{q}_0), \quad \boldsymbol{q}(t| - \boldsymbol{p}_0, \boldsymbol{q}_0) = \boldsymbol{q}(-t|\boldsymbol{p}_0, \boldsymbol{q}_0), \tag{148}$$

(the functions on the RHS of the above equations satisfy the Hamilton equations (99) with initial conditions $(-\boldsymbol{p}_0, \boldsymbol{q}_0)$) we find

$$\langle F_1(t)F_2(0) \rangle = \int d\boldsymbol{p}_0 d\boldsymbol{q}_0 P_{eq}(-\boldsymbol{p}_0, \boldsymbol{q}_0) F_1[-\boldsymbol{p}(-t|\boldsymbol{p}_0, \boldsymbol{q}_0), \boldsymbol{q}(-t|\boldsymbol{p}_0, \boldsymbol{q}_0)]F_2[-\boldsymbol{p}_0, \boldsymbol{q}_0]. \tag{149}$$

If neither a magnetic field nor an angular rotation are present in the system, then the equilibrium state is time-reversal invariant, $P_{eq}(-\boldsymbol{p}_0, \boldsymbol{q}_0) = P_{eq}(\boldsymbol{p}_0, \boldsymbol{q}_0)$. If in addition both dynamical variables are either invariant under time-reversal ($F_i[-\boldsymbol{p}_0, \boldsymbol{q}_0] = F_i[\boldsymbol{p}_0, \boldsymbol{q}_0]$) or both change sign under time-reversal ($F_i[-\boldsymbol{p}_0, \boldsymbol{q}_0] = -F_i[\boldsymbol{p}_0, \boldsymbol{q}_0]$) then we obtain

$$\langle F_1(t) F_2(0) \rangle = \int d\boldsymbol{p}_0 d\boldsymbol{q}_0 P_{eq}(\boldsymbol{p}_0, \boldsymbol{q}_0) F_1[\boldsymbol{p}(-t|\boldsymbol{p}_0, \boldsymbol{q}_0), \boldsymbol{q}(-t|\boldsymbol{p}_0, \boldsymbol{q}_0)] F_2[\boldsymbol{p}_0, \boldsymbol{q}_0] = \langle F_1(0) F_2(t) \rangle, \tag{150}$$

where we used stationarity. It follows that for two variables x_i, x_j with the property above one has $\varphi_{ij}(t) = \varphi_{ji}(t)$ that is the matrix φ_{ij} is symmetric. In the case that one of the variables changes sign under time-reversal while the other does not, one would obtain antisymmetry $\varphi_{ij}(t) = -\varphi_{ji}(t)$. Finally, if magnetic field or angular rotation are present in the system, then $P_{eq}(-\boldsymbol{p}_0, \boldsymbol{q}_0) = P_{eq}(\boldsymbol{p}_0, \boldsymbol{q}_0)$ no longer holds true. However, taking as example the case with a magnetic field $\boldsymbol{H}$, and considering P_{eq} and $\varphi_{ij}(t)$ as functions of $\boldsymbol{H}$, one can generalize the above relations employing $P_{eq}(-\boldsymbol{p}_0, \boldsymbol{q}_0, -\boldsymbol{H}) = P_{eq}(\boldsymbol{p}_0, \boldsymbol{q}_0, \boldsymbol{H})$.

The symmetry of $\varphi_{ij}(t)$ implies by Eq. (145) that $\exp[-t\hat{\lambda}]\hat{\varphi}(0)$ must be a symmetric matrix, where $\hat{\varphi}(0)_{ij} = \langle x_i x_j \rangle$ is symmetric by definition (we designate matrices by hats). The corresponding implication for the coefficients λ_{ij} is expressed most clearly by introducing conjugate thermodynamic forces as follows. We note that the state with given values of x_i is a non-equilibrium state, the partial equilibrium state mentioned before. One can associate a well-defined entropy with this partial equilibrium state which will be a function of x_i only. In the Brownian motion example, this entropy is the entropy of the fluid which hydrodynamic state is imposed by the value of the slow variable so that $S = S(\boldsymbol{v})$. In general, we introduce entropy S as a function of x_i. This function $S(x_1, x_2, .., x_n)$ is maximal at $x_i = 0$ so that its general expression at small x_i is

$$S = S_{eq} - \frac{1}{2}\beta_{ij} x_i x_j, \tag{151}$$

where the positive definite matrix β_{ij} is symmetric. The above quadratic approximation to entropy normally applies in the same range of x_i as the linear approximation to the force given by Eq. (144). We now introduce a thermodynamically conjugate variable to x_i by

$$X_i \equiv -\frac{\partial S}{\partial x_i} = \beta_{ij} x_j. \tag{152}$$

At equilibrium x_i and X_i vanish simultaneously. Now we may rewrite Eq. (143) in terms of X_i as

$$\dot{x}_i = -\gamma_{ij} X_j, \quad \gamma_{ij} = \lambda_{ik} \beta_{kj}^{-1}. \tag{153}$$

The coefficients γ_{ij} are called kinetic coefficients and the Onsager reciprocal relation states that these coefficients are symmetric,

$$\gamma_{ij} = \gamma_{ji}. \tag{154}$$

To see the above relation we note that Eq. (153) by the Onsager hypothesis implies that

$$\varphi_{ij}(t) = (\exp[-t\hat{\gamma}])_{ik} \langle X_k x_j \rangle_{eq}. \tag{155}$$

The crucial observation is that the equilibrium averages $\langle X_k x_j \rangle_{eq}$ obey $\langle X_k x_j \rangle_{eq} = \delta_{kj}$, that the implies Eq. (154) by the equation above and $\varphi_{ij}(t) = \varphi_{ji}(t)$. The latter identity is a consequence of the Einstein formula that states that the probability density function of slow variables in equilibrium satisfies

$$P(x_1, x_2, .., x_n) \propto e^{S(x_1, x_2, .., x_n)} \propto \exp\left[-\frac{1}{2}\beta_{ij} x_i x_j\right]. \tag{156}$$

The formula can be seen as the statement of the microcanonical ensemble that the probability of given values x_i is proportional to the volume of the phase space (or the number of states) corresponding to those values (remind that entropy if the logarithm of the number of states). Introducing $\delta S = -\beta_{ij} x_i x_j / 2$ and normalization factor N one has

$$\langle x_k X_i \rangle = -\frac{1}{N} \int x_k \frac{\partial \delta S}{\partial x_i} e^{\delta S} d\boldsymbol{x} = -\frac{1}{N} \int x_k \frac{\partial}{\partial x_i} e^{\delta S} d\boldsymbol{x} = \delta_{ik}, \tag{157}$$

where we integrated by parts using the normalization of the probability. For the entropy production rate we have

$$\frac{dS}{dt} = \frac{\partial S}{\partial x_i} \dot{x}_i = -X_i \dot{x}_i = \gamma_{ij} X_i X_j. \tag{158}$$

It follows that γ_{ij} must a positive definite matrix. Note also that the above relations are completely symmetric with respect to the exchange of x_i and X_i, one has:

$$S = S_{eq} - \frac{1}{2}\beta_{ij}^{-1}X_iX_j, \quad x_i = -\frac{\partial S}{\partial X_i}, \quad \frac{dS}{dt} = \frac{\partial S}{\partial X_i}\dot{X}_i = -x_i\dot{X}_i. \tag{159}$$

This symmetry reflects that both x_i and X_i can be considered as non-equilibrium coordinates on equal footing.

D. The general fluctuation-dissipation theorem

The linear relaxation equations described above apply at $x_i \gg \langle x_i^2 \rangle^{1/2}$. When x_i become comparable with the typical amplitudes of their thermal fluctuations, one needs to introduce into the equations a random component of the force which does not vanish in equilibrium with $x_i = 0$. This is just like in the case of the Brownian motion. The resulting general Langevin equation reads

$$\frac{d\boldsymbol{x}}{dt} = -\lambda\boldsymbol{x} + \boldsymbol{F}(t), \tag{160}$$

where λ is a matrix with coefficients λ_{ij} and $\boldsymbol{F}$ is a random vector force with pair correlation

$$\langle F_i(t)F_j(t') \rangle = 2B_{ij}\delta(t - t'). \tag{161}$$

Note that by definition B_{ij} is a symmetric matrix. We now determine the amplitude B of the force fluctuations in terms of λ and equilibrium fluctuations of x_i, thus generalizing the fluctuation-dissipation theorem we had for Brownian motion. For a system that approaches equilibrium all eigenvalues of λ must have a positive real part, however they can be complex (cf. the dumbbell model of the polymer considered in class). Then the contribution of the initial conditions in the solution

$$\boldsymbol{x}(t) = e^{-t\lambda}\boldsymbol{x}(0) + \int_0^t ds\, e^{-(t-s)\lambda}\boldsymbol{F}(s) \tag{162}$$

of Eq. (160) decays at large times and the steady state expression for $\boldsymbol{x}$ can be written as

$$\boldsymbol{x} = \int_{-\infty}^t ds\, e^{-(t-s)\lambda}\boldsymbol{F}(s). \tag{163}$$

This leads to the following expression for the equilibrium correlation matrix $M_{ij} \equiv \langle x_i x_j \rangle$:

$$M_{ij} = \int_{-\infty}^t ds \int_{-\infty}^t ds'\, e_{ik}^{-(t-s)\lambda}\langle F_k(s)F_l(s') \rangle e_{lj}^{-(t-s')\lambda^T}, \tag{164}$$

where T stands for the transpose. Averaging the above equation with the help of Eq. (161) and changing the integration variable, we find a matrix relation

$$M = 2\int_0^\infty dt\, e^{-t\lambda}Be^{-t\lambda^T}. \tag{165}$$

To evaluate the time integral we consider the symmetrized matrix $\lambda M + M\lambda^T$ that is given by

$$\lambda M + M\lambda^T = 2\int_0^\infty dt\, \lambda e^{-t\lambda}Be^{-t\lambda^T} + 2\int_0^\infty dt\, e^{-t\lambda}Be^{-t\lambda^T}\lambda^T = -2\int_0^\infty dt\, \frac{d}{dt}e^{-t\lambda}Be^{-t\lambda^T} = 2B,$$

where the contribution of the upper limit of integration vanishes because the eigenvalues of λ all have positive real parts. We find the fluctuation dissipation theorem, which expresses the amplitude of the fluctuations of the random force in terms of matrix of the "friction" coefficients λ and the equilibrium correlation functions M:

$$\lambda M + M\lambda^T = 2B. \tag{166}$$

Note that by their definition as the second moments, both M and B are symmetric while generally λ is not. Using Einstein formula for the probability density function of x_i

$$P(x_1, x_2, .., x_n) = \frac{1}{N}\exp\left[-\frac{1}{2}\beta_{ij}x_ix_j\right], \tag{167}$$

one has $M_{ij} = \beta_{ij}^{-1}$. It follows from the definition of the kinetic coefficients that $(\lambda M)_{ij} = \lambda_{ik}\beta_{kj}^{-1} = \gamma_{ij}$. It follows that

$$B_{ij} = \frac{\gamma_{ij} + \gamma_{ji}}{2}. \tag{168}$$

In the case where time-reversal symmetry implies symmetry of $\langle x_i(t)x_j(0)\rangle$, we have that γ is a symmetric matrix and B is just equal to γ:

$$B_{ij} = \gamma_{ij}, \tag{169}$$

that is the kinetic coefficients give directly the amplitude of fluctuations of the random component of the force.

E. Generalization to fields

Among the most important and interesting applications of the general theory of fluctuations of slow variables near equilibrium is the application to the case where the slow variables experiencing relaxation are fields. An important class of such fields is provided by densities of locally conserved charges, see the next subsection. It is therefore important to generalize the relations of the last subsection to this case. Here part of the indices of the set of slow variables is continuous with spatial points playing the role of these indices. We consider the general case where the slow variable is a vector field $\phi_i(\boldsymbol{x})$. The field relaxation to its equilibrium (mean) value $\phi_i(\boldsymbol{x}) = 0$ is described by the general linear equation

$$\frac{\partial \phi_i(\boldsymbol{x}, t)}{\partial t} = -\int \lambda_{ij}(\boldsymbol{x}, \boldsymbol{x}')\phi_i(\boldsymbol{x}', t)d\boldsymbol{x}'. \tag{170}$$

The expression for entropy in non-equilibrium state defined by a macroscopic deviation of $\phi_i(\boldsymbol{x})$ from equilibrium is given by

$$S = S_{eq} - \frac{1}{2}\int \phi_i(\boldsymbol{x})\beta_{ij}(\boldsymbol{x}, \boldsymbol{x}')\phi_j(\boldsymbol{x}')d\boldsymbol{x}d\boldsymbol{x}', \tag{171}$$

where $\beta_{ij}(\boldsymbol{x}, \boldsymbol{x}')$ is a symmetric kernel. The force $\Phi_i(\boldsymbol{x})$ thermodynamically conjugate to $\phi_i(\boldsymbol{x})$ is

$$\Phi_i(\boldsymbol{x}) = -\frac{\delta S}{\delta \phi_i(\boldsymbol{x})} = \int \beta_{ij}(\boldsymbol{x}, \boldsymbol{x}')\phi_j(\boldsymbol{x}'). \tag{172}$$

We have

$$\langle \phi_i(\boldsymbol{x})\Phi_j(\boldsymbol{x}')\rangle = -\int D\phi \phi_i(\boldsymbol{x})\frac{\delta S}{\delta \phi_i(\boldsymbol{x})}e^{\delta S} = \langle \frac{\delta \phi_i(\boldsymbol{x})}{\delta \phi_j(\boldsymbol{x}')}\rangle = \delta_{ij}\delta(\boldsymbol{x} - \boldsymbol{x}'), \tag{173}$$

where $D\phi$ is a functional integral. If we define linear operator $\hat{\gamma}$ by the equation

$$\frac{\partial \phi_i(\boldsymbol{x}, t)}{\partial t} = -\int \gamma_{ij}(\boldsymbol{x}, \boldsymbol{x}')\phi_i(\boldsymbol{x}')d\boldsymbol{x}' \equiv -\hat{\gamma}\boldsymbol{\Phi}, \quad \gamma_{ij}(\boldsymbol{x}, \boldsymbol{x}') = \int d\boldsymbol{x}'' \lambda_{ik}(\boldsymbol{x}, \boldsymbol{x}'')\beta^{-1}(\boldsymbol{x}'', \boldsymbol{x}'), \tag{174}$$

then the use of the Onsager hypothesis gives

$$\langle \phi_i(\boldsymbol{x}, t)\phi_j(\boldsymbol{x}', 0)\rangle = \exp\left[-t\hat{\gamma}\right](\boldsymbol{x}, \boldsymbol{x}'). \tag{175}$$

If the symmetry properties of $\phi_i(\boldsymbol{x})$ under time-reversal are the same then $\hat{L}$ is a symmetric operator which means that its kernel $\gamma_{ij}(\boldsymbol{x}, \boldsymbol{x}')$ does not change under the interchange of i with j and $\boldsymbol{x}$ with $\boldsymbol{x}'$. Straightforward generalization holds for the cases of different time-reversal properties or to the cases with a magnetic field or an angular rotation.

F. Locally conserved charges as slow variables. Diffusion equation

A very important application of the theory of fluctuations of slow variables is the description of near equilibrium fluctuations of locally conserved charges. A locally conserved charge $\rho(\boldsymbol{x}, t)$ is a field which microscopic equation of motion has a form

$$\frac{\partial \rho(\boldsymbol{x}, t)}{\partial t} + \nabla \cdot \boldsymbol{j}(\boldsymbol{x}, t) = 0, \tag{176}$$

where $\boldsymbol{j}(\boldsymbol{x}, t)$ is called a current. The above equation is a *local* conservation law: it is not only that $\int \rho(\boldsymbol{x}, t)$ is conserved but it is conserved locally. The "amount" of ρ inside any volume V changes only due to the flux through the boundaries

$$\frac{d}{dt} \int_V \rho(\boldsymbol{x}, t) d\boldsymbol{x} = - \int \boldsymbol{j} \cdot d\boldsymbol{S}. \tag{177}$$

Thus, while conservation of the total amount $\int \rho(\boldsymbol{x}, t)$ allows ρ to disappear in one region and reappear in a completely different region, the locality of the conservation law forbids such a possibility: the charge must pass through the intermediate regions. One can say that the charge *flows*. Consider as an example quantum mechanics of a single particle with wave-function ψ. Naturally, $\int |\psi|^2 d\boldsymbol{x}$, which describes the total probability to find the particle anywhere in space is conserved and equal to one. However, its conservation by itself does not guarantee that the particle will not disappear in one region and reappear in another, faraway, region (which would make things look quite like magic), it is the fact that $|\psi|^2$ satisfies a law of the form (176) that guarantees that. Thus locality is a very essential physical property. Other examples of locally conserved charges include densities of mass, electric charge, momentum, energy, spin etc.

Locally conserved charges are natural, universal examples of slow variables. Applying Fourier transform to Eq. (176) one has

$$\frac{\partial \rho(\boldsymbol{k}, t)}{\partial t} = i\boldsymbol{k} \cdot \boldsymbol{j}(\boldsymbol{k}, t). \tag{178}$$

Thus non-equilibrium perturbations of a locally conserved charge which have a sufficiently long-wavelength (small k) will always decay slowly. Hence these are slow variables and the theory we described above should apply to them. As a first example of the use of the theory let us consider a fluid of particles where each particle carries a definite value of magnetic moment along some fixed axis. It is assumed that the magnetic moment of each particle is not changed by interactions with other particles. Then the (locally conserved) density of magnetic momentum is

$$\rho(\boldsymbol{x}, t) = \sum_{i=1}^{N} m_i \delta[\boldsymbol{x} - \boldsymbol{x}_i(t)] \tag{179}$$

where particles magnetic momenta m_i obey $m_i = \pm|m|$ and the total magnetic moment is zero, $\sum m_i = 0$. If we now create say a periodic perturbation of $\rho(\boldsymbol{x}, 0)$ in space such that the wavelength is sufficiently large then the relaxation of this perturbation is going to be slow. More generally, we may consider $\rho(\boldsymbol{x}, 0)$ such that its Fourier image is supported mainly at small wave numbers. We consider near equilibrium fluctuations in the range where linear decay law holds while the fluctuating component of the "force" can be neglected. The theory of slow variables says then that $\rho(\boldsymbol{x}, t)$ satisfies a closed equation which signifies that $\boldsymbol{j}(\boldsymbol{x}, t)$ should be expressible in terms of $\rho(\boldsymbol{x}, t)$. The corresponding relation between $\boldsymbol{j}$ and ρ is called a constitutive relation. Since the equations on ρ must be linear, the most general form of the constitutive relation is

$$j_i(\boldsymbol{x}, t) = \int d\boldsymbol{x}' K_i(\boldsymbol{x}, \boldsymbol{x}') \rho(\boldsymbol{x}', t) \tag{180}$$

where K is some kernel which due to the spatial homogeneity of the equilibrium state depends only on the difference of coordinates, $K_i(\boldsymbol{x}, \boldsymbol{x}') = K_i(\boldsymbol{x} - \boldsymbol{x}')$. Since in equilibrium with $\rho(\boldsymbol{x}, t) = const$ there must be no current we have

$$\int d\boldsymbol{x} K_i(\boldsymbol{x}) = 0. \tag{181}$$

While some exceptions to the equation above are possible (where the current has a non-vanishing constant component), in general the equation holds true. We now make an assumption, which is normally true, that the kernel K has some finite range l (if there are fluctuations of ρ far away, the current here can be neglected). Then for sufficiently long wavelength perturbations of ρ with $\lambda \gg l$, the Taylor expansion of ρ in the integrand will produce the leading order expression for $\boldsymbol{j}(\boldsymbol{x}, t)$ in the small parameter l/λ. We have

$$j_i(\boldsymbol{x}, t) = \int d\boldsymbol{x}' K_i(\boldsymbol{x} - \boldsymbol{x}') \left[\rho(\boldsymbol{x}, t) + (\boldsymbol{x}'_j - \boldsymbol{x}_j) \nabla_j \rho(\boldsymbol{x}, t) + .. \right] \approx -D_{ij} \nabla_j \rho(\boldsymbol{x}, t), \quad D_{ij} \equiv \int K_i(\boldsymbol{x}) x_j d\boldsymbol{x} \tag{182}$$

where we took into account Eq. (181). If in addition the system is isotropic then $K_i(\boldsymbol{x}) = x_i K(|\boldsymbol{x}|)$ and $D_{ij} = D\delta_{ij}$. We conclude that for isotropic system with a kernel K vanishing fast outside a finite range of interactions, the current associated with a slowly varying in space, non-equilibrium distribution of concentration is

$$\boldsymbol{j}(\boldsymbol{x}, t) = -D\nabla \rho(\boldsymbol{x}, t). \tag{183}$$

The above expression can be understood as follows. When the field ρ relaxes to its equilibrium value, it does so slowly, so that the rest of variables of the system are enslaved by ρ, in particular, the current $\boldsymbol{j}$. This current should determined by ρ locally because the exchange of ρ between different parts of the system takes place locally. As the gradients of ρ are small, it is enough to take the first nonvanishing term in the expansion in the powers of the gradient which has the general form $-D\nabla\rho$ with some coefficient ρ. The above expression for the current leads to the diffusion equation for ρ,

$$\frac{\partial \rho}{\partial t} = D\nabla^2 \rho, \tag{184}$$

so that we recognize that D is in fact the diffusion coefficient of magnetic momentum. For the low wave-number Fourier components of ρ, which are the slow variables behind the treatment, the above equation implies that

$$\frac{\partial \rho(\boldsymbol{k}, t)}{\partial t} = -Dk^2 \rho(\boldsymbol{k}, t), \quad kl \ll 1. \tag{185}$$

The above equation is completely analogous to the equation $\dot{x} = -\lambda x$ on a single slow variable x. In fact, we could write $\partial_t \rho(\boldsymbol{k}, t) = -\lambda(k)\rho(\boldsymbol{k}, t)$ as a particular case of the general equation (143) without any preliminary treatment - the excitation of $\rho(\boldsymbol{k})$ does not lead to an excitation of other Fourier harmonics of ρ by the spatial homogeneity. Indeed, the latter implies that the general form of the equation on ρ is $\partial_t \rho(\boldsymbol{x}, t) = \int \lambda(\boldsymbol{x} - \boldsymbol{x}')\rho(\boldsymbol{x}', t)d\boldsymbol{x}'$ which Fourier transform is $\partial_t \rho(\boldsymbol{k}, t) = -\lambda(k)\rho(\boldsymbol{k}, t)$. Now just as the equation $\dot{x} = -\lambda x$ holds only for x in the range $\langle x^2 \rangle^{1/2} \ll |x| \ll x_{nlin}$ where x_{nlin} gives the limit of applicability of linear approximation to the relaxation, so Eq. (185) holds for $\langle |\rho(\boldsymbol{k})|^2 \rangle \ll |\rho(\boldsymbol{k})| \ll \rho_{nlin}(\boldsymbol{k})$, where $\rho_{nlin}(\boldsymbol{k})$ is the limit of applicability of linear approximation.

The non-trivial information contained in the diffusion equation is that the leading order behavior of $\lambda(k)$ at small k is $\lambda(k) = Dk^2$. Clearly, this has the form of the leading order term in the Taylor expansion of $\lambda(k)$ that takes into account $\lambda(k = 0) = 0$, where the latter demand is a consequence of the exact dynamical equation (178). We observe that diffusion equation should hold, as it does indeed, in a great variety of situations. It provides a universal description of a linearized decay of a scalar field, which zero wave-number Fourier is conserved, under the assumption of spatial homogeneity and isotropy (the latter demand, leading to $\lambda'(k = 0) = 0$, ensures that the first order term in the Taylor expansion of $\lambda(k)$ vanishes). An additional, most crucial assumption here is that $\lambda(k)$ is analytic at $k = 0$, which is by no means evident. Note that the physical meaning of the approximation $\lambda(k) \approx Dk^2$ is easier understood in real space, where one sees that the condition of small k is $kl \ll 1$ where l is the range of the current kernel.

Equation (185) implies that the Fourier harmonics of $\rho(\boldsymbol{r}, t)$ decay exponentially according to

$$\rho(\boldsymbol{k}, t) = \exp[-t/\tau_k]\rho(\boldsymbol{k}, 0), \quad \tau_k = (Dk^2)^{-1}. \tag{186}$$

Thus $\rho(\boldsymbol{k}, t)$ relaxes within a characteristic time-scale $(Dk^2)^{-1}$ becoming infinite at $k \to 0$. The relaxation leads to a state where only $\rho(k = 0)$ is present, corresponding to homogeneous distribution in space. The above implies an additional constraint on k for Eq. (185) to hold. This follows from the consistency demand that states that the relaxation time of the slow variable $(Dk^2)^{-1}$ is much larger then the relaxation time τ_{rel} of the fast variables to the partial equilibrium state determined by $n(\boldsymbol{r})$. The time-scale τ_{rel} is a characteristic time-scale of molecular dynamics. Considering as an example a system of classical particles with mass m which interact via a pair potential of strength ϵ and range a, one obtains by dimensional arguments that $\tau_{rel} \sim a(m/\epsilon)^{1/2}$ (which typically produces numbers like 10^{-12} seconds, i. e. vanishingly small on a macroscopic time-scale). Thus Eq. (185) must be supplemented by the condition $(Dk^2)^{-1} \gg \tau_{rel}$. The condition always becomes true at a sufficiently small k, demonstrating again the self-consistency of the analysis.

The description of the relaxation of $\rho(\boldsymbol{r}, t)$ in real space is left for the exercise. Here we only provide the basic solution of the diffusion equation that describes the decay of the initial perturbation $\rho(\boldsymbol{r}, 0) = \rho_0 \delta(\boldsymbol{r})$ localized at a point. The solution of the diffusion equation with this initial condition is

$$\rho(\boldsymbol{r}, t) = \frac{\rho_0}{(4\pi D t)^{3/2}} \exp\left[-\frac{r^2}{4Dt}\right]. \tag{187}$$

The solution describes a *self-similar* decay of the perturbation where density profile at a later time can be obtained from the profile at an earlier time by mere rescaling of the coordinates on both axes.

Finally, in the case of density, the property that $\rho(\boldsymbol{k}, t)$ is a slow variable at small k can be also seen by noting that $\rho(\boldsymbol{k})$ is formed by spatial perturbations with characteristic scale k^{-1}. Such perturbations involve typically about $\langle \rho \rangle k^{-3}$ particles. At small k this number of particles is large saying that $\rho(\boldsymbol{k})$ characterizes so to say "heavy", and thus slow, perturbations of large numbers of particles.

G. Spin correlation function and Kubo formula for diffusion coefficient

By the Onsager hypothesis the diffusion equation that describes the decay of small perturbations from equilibrium, also describes the decay of the equilibrium correlation function. Here we establish the corresponding form of the correlation function and derive the so-called Kubo formula for the diffusion coefficient D. For clarity, we specify to a particular kind of density, the magnetization density $M(\boldsymbol{r}, t)$ defined by

$$M(\boldsymbol{r}, t) = \sum_i m_i \delta\left[\boldsymbol{r} - \boldsymbol{r}_i(t)\right]. \tag{188}$$

It is assumed that particle interactions conserve m_i so that differentiating over time we obtain the local conservation law

$$\frac{\partial M}{\partial t} = -\nabla \cdot \boldsymbol{j}^M, \quad \boldsymbol{j}^M \equiv \sum_i m_i \frac{d\boldsymbol{r}_i}{dt} \delta\left[\boldsymbol{r} - \boldsymbol{r}_i(t)\right], \tag{189}$$

where $\boldsymbol{j}^M$ is the magnetic current. We now consider equilibrium fluctuations of $M(\boldsymbol{r}, t)$ and, in particular, the spin correlation function

$$S(\boldsymbol{r}, t) \equiv \langle M(\boldsymbol{r}, t) M(0, 0) \rangle. \tag{190}$$

At equilibrium $\langle M \rangle = 0$ so that $S(\boldsymbol{r}, t)$ characterizes the fall of correlations in M with space and time separations. For example the equal time correlation function $S(\boldsymbol{r}, t = 0) = \langle M(\boldsymbol{r}) M(0) \rangle$ is expected to decay fast at $r \gg l_{cor}$ where l_{cor} is a finite correlation range of magnetization fluctuations.

Let us note that (long-wavelength) equilibrium fluctuations of $M(\boldsymbol{r}, t)$ can be represented as a sum of *independent* fluctuations of $M(\boldsymbol{k}, t)$, that is the random variables $M(\boldsymbol{k}, t)$ in $M(\boldsymbol{r}, t) = \int M(\boldsymbol{k}, t) \exp[i\boldsymbol{k} \cdot \boldsymbol{r}] d\boldsymbol{k}/(2\pi)^d$ are independent. The statistical independence of different Fourier harmonics is a consequence of spatial homogeneity which implies that $\langle M(\boldsymbol{k}, t) M^*(\boldsymbol{k}', 0) \rangle \propto \delta(\boldsymbol{k} - \boldsymbol{k}')$ [here the superscript $*$ stands for complex conjugation and we used $M(-\boldsymbol{k}) = M^*(\boldsymbol{k})$]. Noting that according to the Einstein formula the probability density functional (PDF) of $M(\boldsymbol{k}, t)$ is Gaussian [the PDF is proportional to the exponent of entropy S where

$$S = S_{eq} - \frac{1}{2} \int \beta(\boldsymbol{x} - \boldsymbol{x}') M(\boldsymbol{x}) M(\boldsymbol{x}') d\boldsymbol{x} d\boldsymbol{x}' = S_{eq} - \frac{1}{2} \int \frac{d\boldsymbol{k}}{(2\pi)^d} \beta(\boldsymbol{k}) M*(\boldsymbol{k}) M(\boldsymbol{k}), \tag{191}$$

cf. Eq. (171)] and that $\langle M(\boldsymbol{k}) \rangle = 0$ we conclude that $M(\boldsymbol{k})$ with different $\boldsymbol{k}$ are independent. Thus consideration of the correlation function $S(\boldsymbol{r}, t)$ is performed easier in the Fourier space. We introduce

$$S(\boldsymbol{k}, t) = \int e^{-i\boldsymbol{k} \cdot \boldsymbol{r}} \langle M(\boldsymbol{r}, t) M(0, 0) \rangle. \tag{192}$$

The Onsager hypothesis and Eq. (185) imply that

$$\frac{\partial S(\boldsymbol{k}, t)}{\partial t} = -Dk^2 S(\boldsymbol{k}, t), \quad kl \ll 1, \tag{193}$$

so that

$$S(\boldsymbol{k}, t) = \exp[-Dk^2|t|] S(\boldsymbol{k}, 0), \quad kl \ll 1, \tag{194}$$

where we used that $S(\boldsymbol{r}, t)$ must be an even function of t because it represents correlation of two variables with the same transformation rule under the time-reversal. We observe that to find $S(\boldsymbol{k}, t)$ we need to know $S(\boldsymbol{k}, 0)$ at small k. The latter can be expressed with the help of the magnetic susceptibility χ defined by

$$\chi = \frac{\partial \langle M \rangle_h}{\partial h_{|h=0}}, \tag{195}$$

where $\langle M \rangle_h$ is the average value of the magnetic moment in the presence of the magnetic field h. This average can be determined by methods of the equilibrium statistical mechanics. We note that in the presence of the magnetic field h the Hamiltonian of the system is given by $H' = H - M_{tot}h$ where H is the system Hamiltonian at $h = 0$ and M^{tot} is the total magnetic moment of the system. Note that $\langle M \rangle = \langle M_{tot} \rangle / V$ so that we have

$$\chi = \frac{\partial}{\partial h_{|h=0}} \frac{1}{V} \frac{tr M_{tot} \exp[-\beta H + \beta M_{tot}h]}{tr \exp[-\beta H + \beta M_{tot}h]} = \frac{\beta}{V} \frac{tr M_{tot}^2 \exp[-\beta H]}{tr \exp[-\beta H]} = \frac{\beta \langle M_{tot}^2 \rangle}{V}, \tag{196}$$

where we used that

$$\frac{trM_{tot}\exp[-\beta H]}{tr\exp[-\beta H]} = \langle M_{tot}\rangle_{eq} = 0. \tag{197}$$

Using $M_{tot} = \int M(\boldsymbol{r})d\boldsymbol{r}$ we obtain

$$\chi = \frac{\beta}{V}\int\langle M(\boldsymbol{r}_1)M(\boldsymbol{r}_2)\rangle d\boldsymbol{r}_1 d\boldsymbol{r}_2 = \frac{\beta}{V}\int S(\boldsymbol{r}_1-\boldsymbol{r}_2,0)d\boldsymbol{r}_1 d\boldsymbol{r}_2 = \beta\int S(\boldsymbol{r},0)d\boldsymbol{r} = \beta S(k=0,0). \tag{198}$$

Thus we obtain that for k^{-1} much larger than the scale l_{cor} beyond which $S(\boldsymbol{r},0)$ decays, we have

$$S(\boldsymbol{k},0) \approx S(k=0,0) = \chi k_B T, \tag{199}$$

where we assumed that $S(\boldsymbol{k},0)$ is analytic at $k=0$. Since normally the static correlation length l_{cor} is smaller or of the order of the dynamic correlation length l, then we shall assume that Eq. (199) holds in the range $kl \ll 1$ which produces

$$S(\boldsymbol{k},t) = \exp[-Dk^2|t|]\chi k_B T, \quad kl \ll 1. \tag{200}$$

The above formula describes the decay of correlations of $M(\boldsymbol{k},t)$ and it has the same form of purely exponential decay as the correlation function of the velocity of a Brownian particle. For $S(\boldsymbol{k},\omega) = \int S(\boldsymbol{k},t)\exp[i\omega t]dt$ we find

$$S(\boldsymbol{k},\omega) = 2\chi k_B T\frac{Dk^2}{(Dk^2)^2+\omega^2}, \quad kl \ll 1, \tag{201}$$

which is proportional to the spectrum of fluctuations of $M(\boldsymbol{k},t)$. The above formula has the same form as the spectrum of velocity of a Brownian particle with τ substituted by the relaxation time $(Dk^2)^{-1}$ of $M(\boldsymbol{k},t)$. Let us note that even though the expression (201) can be expected to correspond to the asymptotic form of $S(\boldsymbol{k},\omega)$ at small k and ω, it does not have a simple analytic behavior at small k and ω:

$$\lim_{k\to 0}\lim_{\omega\to 0}S(\boldsymbol{k},\omega) = \infty, \quad \lim_{\omega\to 0}\lim_{k\to 0}S(\boldsymbol{k},\omega) = 0, \tag{202}$$

that is the limits don't commute. It is possible to express $S(\boldsymbol{k},\omega)$ in terms of another object that already has a nice analytic properties at small k and ω - this is the content of the so-called dispersion relation representation which is beyond our scope here.

We note the following representation of the diffusion coefficient

$$D\chi = \frac{\beta}{2}\lim_{\omega\to 0}\lim_{k\to 0}\frac{\omega^2}{k^2}S(\boldsymbol{k},\omega). \tag{203}$$

Despite the apparent emptiness of the above relation, its elaboration allows one to obtain an important Kubo formula for the diffusion coefficient. Performing Fourier transform of Eq. (189) both over spatial and temporal coordinates we find $M(\boldsymbol{k},\omega) = -\boldsymbol{k}\cdot j^M(\boldsymbol{k},\omega)/\omega$ (here we don't need to deal with the possible boundary terms as we plan to use the relation for the spectra). It follows that the magnetic current spectrum $E_{ij}(\boldsymbol{k},\omega)$, defined by

$$E_{ij}(\boldsymbol{k},\omega) = \int d\boldsymbol{r}dt\exp[i\omega t - i\boldsymbol{k}\cdot\boldsymbol{r}]\langle j_i(\boldsymbol{r},t)j_j(0,0)\rangle, \tag{204}$$

satisfies

$$\frac{k_i k_j}{\omega^2}E_{ij}(\boldsymbol{k},\omega) = S(\boldsymbol{k},\omega) = 2\chi k_B T\frac{Dk^2}{(Dk^2)^2+\omega^2}, \quad kl \ll 1. \tag{205}$$

Isotropy implies that the leading order term in $E_{ij}(\boldsymbol{k},\omega)$ at small k is $E_{ij}(\boldsymbol{k},\omega) = E_{ll}\delta_{ij}/3$ which leads to

$$\frac{E_{ll}(\boldsymbol{k},\omega)}{3} = 2\chi k_B T\frac{D\omega^2}{(Dk^2)^2+\omega^2}, \quad kl \ll 1. \tag{206}$$

We find

$$D\chi = \frac{\beta}{2}\lim_{\omega\to 0}\lim_{k\to 0}\frac{E_{ll}(\boldsymbol{k},\omega)}{3} = \frac{1}{3k_B T}\lim_{\omega\to 0}\int_0^\infty e^{i\omega t}dt\int d\boldsymbol{r}\langle \boldsymbol{j}^M(\boldsymbol{r},t)\cdot\boldsymbol{j}^M(0,0)\rangle. \tag{207}$$

where we used the definition (204) and assumed that the limit $k \to 0$ is regular, i. e. equal to the value of the expression at $k = 0$ (which is not necessarily true for $\omega \to 0$ limit). The above formula can be rewritten by introducing the total magnetic current

$$\boldsymbol{J}^M(t) = \int \boldsymbol{j}^M(\boldsymbol{r}, t) d\boldsymbol{r}. \tag{208}$$

We have

$$\frac{1}{2}\langle[\boldsymbol{J}^M(t), \boldsymbol{J}^M(0)]_s\rangle = V \int \langle \boldsymbol{j}^M(\boldsymbol{r}, t) \cdot \boldsymbol{j}(0, 0)\rangle d\boldsymbol{r}, \tag{209}$$

where $\boldsymbol{J}^M$ on the LHS should be considered as a quantum operator and we defined the symmetrization operation so that

$$[\boldsymbol{J}^M(t), \boldsymbol{J}^M(0)]_s = \boldsymbol{J}^M(t) \cdot \boldsymbol{J}^M(0) + \boldsymbol{J}^M(0) \cdot \boldsymbol{J}^M(t). \tag{210}$$

The equality (215) between a quantum mechanical expression and a classical one holds because the average is determined by low wave-number components of $\boldsymbol{j}(\boldsymbol{k}, t)$ which have classical behavior. The symmetrization is needed to avoid a non-physical imaginary part in the final expression that reads

$$D\chi = \lim_{\omega \to 0} \frac{1}{3Vk_BT} \int_0^\infty e^{i\omega t} dt \frac{1}{2}\langle[\boldsymbol{J}^M(t), \boldsymbol{J}^M(0)]_s\rangle. \tag{211}$$

The above formula is the Kubo formula for the diffusion coefficient. It expresses D in terms of the equilibrium fluctuations of the current and it is an example of the fluctuation-dissipation theorem. The Kubo derivation of the formula uses the linear response theory not considered here. While for slow variables, one can perform a derivation similar to the above to get the Kubo formula, the linear response theory allows to deal with variables which are not necessarily slow and thus is more general in this respect.

VI. HYDRODYNAMIC FLUCTUATIONS

One of the applications of the theory of the dynamics of slow variables near equilibrium, which is of most universal nature, is the theory of hydrodynamic fluctuations. This theory describes both equilibrium fluctuations and relaxation to equilibrium in a wide variety of gases and liquids corresponding to a normal fluid. A normal fluid is a thermodynamic system with the macroscopic fluid behavior that has the property that the only slow variables with arbitrarily large relaxation times are provided by the low wave-number components of the densities of mass, momentum and energy. The symmetries of spatial homogeneity and isotropy are assumed. It should be stressed that the theory described below applies universally to a large class of gases and liquids independently of the details of their molecular interactions.

The signature of a normal fluid is a particular form of the so-called dynamical structure factor $S_{\rho\rho}(\boldsymbol{k}, \omega)$ defined by

$$S_{\rho\rho}(\boldsymbol{k}, \omega) = \int_{-\infty}^\infty dt \int d\boldsymbol{r} e^{i\omega t - i\boldsymbol{k}\cdot\boldsymbol{r}}\langle\langle\rho(\boldsymbol{r}, t)\rho(0, 0)\rangle\rangle, \tag{212}$$

where ρ is the mass density of the fluid and the double angular brackets stand for the dispersion. Here and below we shall put the fluid particle mass equal to unity - in the end of the calculations the mass can be restored by dimensional considerations. Note that $S(\boldsymbol{k}, \omega)$ is a positive function. To show this one uses an identity that we shall use a lot and so we provide it generally - for any two fields f and g, like the densities of conserved charges, we have by the spatial homogeneity that

$$\langle f(\boldsymbol{k}, t)g(-\boldsymbol{k}, 0)\rangle = \int d\boldsymbol{r}d\boldsymbol{r}' \exp[-i\boldsymbol{k}\cdot(\boldsymbol{r} - \boldsymbol{r}')]\langle f(\boldsymbol{r}, t)g(\boldsymbol{r}', 0)\rangle = V \int d\boldsymbol{r} \exp[-i\boldsymbol{k}\cdot\boldsymbol{r}]\langle f(\boldsymbol{r}, t)g(0, 0)\rangle, \quad (213)$$

where V is the system volume. It is easy to see from the above that $S(\boldsymbol{k}, \omega)$ is proportional to the spectrum of fluctuations of $\rho(\boldsymbol{k}, t)$ and as such it must be non-negative. The importance of the dynamical structure factor is that it is directly accessible via neutron or light scattering experiments. One finds that for any normal fluid a universal form of $S_{\rho\rho}(\boldsymbol{k}, \omega)$ as a function of ω holds at small k. This form consists of three peaks - one centered at $\omega = 0$ (Rayleigh peak) and two symmetric peaks (Brillouin peaks) centered at $\omega = \pm c_s k$ where c_s is the speed of sound. All peaks have Lorentzian shape with width proportional to k^2. This width describing the finite life time of the

corresponding excitation that grows as k^{-2} at small k is a signature of hydrodynamic processes, cf. the discussion of diffusion in the previous section. PICTURE

At the late stage of relaxation to equilibrium in normal fluids the only remaining variables out of equilibrium are the low wave-number components of the densities of mass, momentum and energy. The rest of the system is in the partial equilibrium state with respect to these slow variables. To see this consider the relaxation to equilibrium from an arbitrary initial state. First, dynamical variables mix fast locally leading to the system relaxation to the local equilibrium state characterized by the local density, momentum and energy. The latter variables are forbidden to relax locally due to the local conservation law satisfied by them. The relaxation of the densities of the mass, momentum and energy happens only due to their exchange between spatially separated parts of the fluid. Such exchange involves transport of densities in space and it is associated with a long time-scale as compared to the time-scale of relaxation to local equilibrium. The exchange gradually erases perturbations in the densities starting with the smaller wavelength perturbations that demand transport over a smaller scale and occur faster. At a certain stage only perturbations with very small wavenumbers remain and these can be described by hydrodynamics as explained below. Thus hydrodynamics provides universal description of the late stage of relaxation in fluids.

The conservation laws of the mass density ρ, the momentum density $\boldsymbol{g}$ and the energy density E read

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \boldsymbol{g} = 0, \quad \frac{\partial g_i}{\partial t} + \frac{\partial \tau_{ij}}{\partial x_j} = 0, \quad \frac{\partial E}{\partial t} + \nabla \cdot \boldsymbol{j}^E = 0, . \tag{214}$$

where τ_{ij} is the momentum flux tensor and $\boldsymbol{j}^E$ is the energy flux. In the Fourier space Eqs. (214) take the form

$$\frac{\partial \rho(\boldsymbol{k}, t)}{\partial t} + i\boldsymbol{k} \cdot \boldsymbol{g}(\boldsymbol{k}, t) = 0, \quad \frac{\partial g_i(\boldsymbol{k}, t)}{\partial t} + i k_j \tau_{ij}(\boldsymbol{k}, t) = 0, \quad \frac{\partial E(\boldsymbol{k}, t)}{\partial t} + i\boldsymbol{k} \cdot \boldsymbol{j}^E(\boldsymbol{k}, t) = 0. \tag{215}$$

According to the theory of fluctuations of slow variables the slow variables satisfy closed equations so that at sufficiently small k the currents $\boldsymbol{g}(\boldsymbol{k}, t)$, $\tau_{ij}(\boldsymbol{k}, t)$ and $\boldsymbol{j}^E(\boldsymbol{k}, t)$ must be expressible in terms of the slow variables ρ, $\boldsymbol{g}$ and E. As mentioned already, the corresponding relation is called a constitutive relation. Notably the density current $\boldsymbol{g}$ is by itself a conserved quantity and it does not need any additional constitutive relation: one can say that microscopic and macroscopic laws coincide in the case of the continuity equation (the equation on ρ). To address the form of the constitutive relations for τ_{ij} and $\boldsymbol{j}^E$ we note that after the use of the constitutive relations the general equation describing the relaxation of Fourier harmonics of ρ, $\boldsymbol{g}$ and E would take the form

$$\frac{\partial x_i(\boldsymbol{k}, t)}{\partial t} = \lambda_{ij}(\boldsymbol{k}) x_j(\boldsymbol{k}, t), \tag{216}$$

where $x_1(\boldsymbol{k}, t) = \rho(\boldsymbol{k}, t)$, $x_2(\boldsymbol{k}, t) = E(\boldsymbol{k}, t)$ and $x_i(\boldsymbol{k}, t) = g_{i-2}(\boldsymbol{k}, t)$ for $i = 3, 4, 5$. The above form is implied by the spatial homogeneity, see the corresponding discussion in the derivation of the diffusion equation. Note that x_i and λ_{ij} are generally complex. Assuming that the currents have no singularity at $k = 0$ we conclude immediately from Eq. (215) that $\lambda_{ij}(k = 0) = 0$. Like in the case of the diffusion equation we wish to describe the relaxation process to leading order in k assuming the latter is small. While in the case of the diffusion equation the isotropy implied that $\lambda(k)$ is a function of $|\boldsymbol{k}|$ only and thus its derivative must vanish at the origin in $k-$space, $\lambda'(k = 0) = 0$, here λ_{ij} may contains tensors including $\boldsymbol{k}$ and thus depend not only on the magnitude of $\boldsymbol{k}$ but also on its direction. As a result the derivatives of $\lambda_{ij}(\boldsymbol{k})$ do not vanish at the origin generally and the leading order term in the Taylor expansion of $\lambda_{ij}(\boldsymbol{k})$ at small k is $\lambda_{ij} = C_{ijl} k_l$ with constant coefficients $C_{ijl} = \partial_l \lambda_{ij}(k = 0)$. Let us determine these coefficients.

A. Linearized equations of hydrodynamics to first order in derivatives

It is convenient to perform the consideration in real space. The equation $\dot{x}_i = C_{ijl} x_j k_l$ after the inverse Fourier transform produces a linear equation on $\rho(\boldsymbol{x}, t)$, $\boldsymbol{g}(\boldsymbol{x}, t)$ and $E(\boldsymbol{x}, t)$ which is local in space and contains spatial derivatives of the fields of order not higher than the first one. Equations (214) then imply that this approximation corresponds to expressing τ_{ij} and $\boldsymbol{j}^E$ in terms of the local values of ρ, $\boldsymbol{g}$ and E. To introduce the expressions it is convenient to introduce the momentum and the energy per unit mass of the fluid, $\boldsymbol{v}$ and ϵ respectively, via

$$\boldsymbol{v}(\boldsymbol{r}, t) \equiv \frac{\boldsymbol{g}(\boldsymbol{r}, t)}{\rho(\boldsymbol{r}, t)}, \quad \epsilon \equiv \frac{E(\boldsymbol{r}, t)}{\rho(\boldsymbol{r}, t)}. \tag{217}$$

Note that $\boldsymbol{v}$ is nothing but the local velocity of the fluid. The passage from ρ, $\boldsymbol{g}$ and E to ρ, $\boldsymbol{v}$ and ϵ is one to one and we may consider now the expressions for τ_{ij} and $\boldsymbol{j}^E$ in terms of ρ, $\boldsymbol{v}$ and ϵ. These expressions are

$$\tau_{ij} = p\delta_{ij}, \quad \boldsymbol{j}^E = (\rho\epsilon + p)\boldsymbol{v}, \tag{218}$$

where p is the pressure which is determined in terms of ρ and ϵ via the thermodynamic equation of state. Let us explain the above expressions, first providing a physical explanation and then a more formal one. The above expressions for the currents imply [cf. Eq. (177)] that the time derivatives of the momentum and the energy within some volume of the fluid are given by

$$\frac{\partial}{\partial t} \int_V \rho(\boldsymbol{r},t)\boldsymbol{v}(\boldsymbol{r},t)d\boldsymbol{r} = -\int pd\boldsymbol{S}, \quad \frac{\partial}{\partial t} \int_V \rho(\boldsymbol{r},t)\epsilon(\boldsymbol{r},t)d\boldsymbol{r} = -\int (\rho\epsilon + p)\boldsymbol{v} \cdot d\boldsymbol{S}. \tag{219}$$

The first equation simply says that the momentum within the volume changes due to the force that the rest of the fluid exerts on this volume. The second equation says that the energy inside the volume changes due to the power of the force and due to the fluid flux out of the volume, that carries the energy away convectively. In principle, in the momentum equation the convective flux term should be present also, but the term is quadratic in v and it should be discarded within the frame of our consideration.

A more formal argument for the validity of Eq. (221) is based on the Galilean invariance that holds for the considered non-relativistic motions. The local nature of the expressions for the currents and their independence of the spatial derivatives of the fields allows to conclude that the same expressions would hold for a fluid occupying infinite space and moving at a speed $\boldsymbol{v}$. Then Galilean invariance allows to fix the form of the tensors based on the realization that in the frame where the fluid is at rest we have no macroscopic flux of energy, $\boldsymbol{j}^{0,E} = 0$, while the inner stresses in the fluid are described by $\tau_{ij}^0 = p\delta_{ij}$ (here the superscript 0 stands for the rest frame). The latter formula expresses that the only possible form of τ_{ij} that would not produce infinite accelerations in the fluid is where τ_{ij} is proportional to the unit tensor with pressure as the proportionality coefficient (Pascal's law). Then the expressions for τ_{ij} and $\boldsymbol{j}^E$ in the laboratory frame are obtained from the laws of transformations of these tensors under Galilean transformation

$$\tau_{ij} = \tau_{ij}^0 + v_i g_j^0 + v_j g_i^0 + v_i v_j \rho^0, \quad j_i^E = j_i^0 + v_j[\tau_{ij}^0 + \rho^0\epsilon^0\delta_{ij}] + v_i v_j g_j^0 + \frac{1}{2}v^2(g_i^0 + v_i\rho^0). \tag{220}$$

The above laws together with $\boldsymbol{g}^0 = 0$ allow to derive Eq. (221) up to the terms quadratic terms in $\boldsymbol{v}$ that should be discarded. The proof of the above laws of transformation is left for the exercise.

What is the physics described by the considered, lowest order approximation of the dynamics? To see this let us consider the resulting dynamics. We note that to the lowest non-vanishing order in the small amplitude of the perturbations we must set $\rho\boldsymbol{v} \approx \rho_0\boldsymbol{v}$ and $\boldsymbol{j} \approx (\rho_0\epsilon_0 + p_0)\boldsymbol{v}$ because $\boldsymbol{v}$ is small. Here the subscript 0 stand for the equilibrium values of the considered quantities. The resulting equations read

$$\frac{\partial \delta\rho}{\partial t} = -\rho_0\nabla \cdot \boldsymbol{v}, \quad \rho_0\frac{\partial v}{\partial t} = -\nabla p, \quad \rho_0\frac{\partial \epsilon}{\partial t} + \epsilon_0\frac{\partial \rho}{\partial t} = -(\rho_0\epsilon_0 + p_0)\nabla \cdot \boldsymbol{v}, \tag{221}$$

where $\delta\rho \equiv \rho - \rho_0$. The above equations are linearized equations of the so-called ideal hydrodynamics. To realize the meaning of the equations above we use the thermodynamic relation $d\epsilon = Tds - pdV = Tds + pd\rho/\rho^2$ for unit mass of the fluid, where $V = 1/\rho$ and s is the entropy per unit mass. This relation gives

$$\rho T\frac{\partial s}{\partial t} = \rho\frac{\partial \epsilon}{\partial t} - \frac{p}{\rho}\frac{\partial \rho}{\partial t} = -(\rho_0\epsilon_0 + p_0)\nabla \cdot \boldsymbol{v} - \epsilon_0\frac{\partial \rho}{\partial t} - \frac{p_0}{\rho_0}\frac{\partial \rho}{\partial t} = -(\rho_0\epsilon_0 + p_0)\nabla \cdot \boldsymbol{v} + (\rho_0\epsilon_0 + p_0)\nabla \cdot \boldsymbol{v} = 0. \tag{222}$$

Thus the entropy per unit mass is conserved in the considered approximation! Naturally created perturbations (i. e. mechanical perturbations not involving transfer of heat to the fluid) in this approximation do not change the entropy density that remains uniform throughout the fluid. Let us stress that the entropy per unit volume, given by ρs is not uniform. For example if perturbation replaces mechanically part of the fluid to another place, this does not change the entropy per unit mass but it does change the entropy per unit volume. Thus within this approximation, normally one has $s = const$ which leads to

$$\nabla p = \left(\frac{\partial p}{\partial \rho}\right)_s \nabla\delta\rho. \tag{223}$$

The above relation allows to close the first two equations in Eq. (221). Differentiating the equation on density over time, one finds that $\delta\rho$ satisfies the wave equation

$$\frac{\partial^2\delta\rho}{\partial t^2} = \nabla^2 p = \left(\frac{\partial p}{\partial \rho}\right)_s \nabla^2\delta\rho, \tag{224}$$

describing propagation of waves at speed

$$c_s = \sqrt{\left(\frac{\partial p}{\partial \rho}\right)_s}. \tag{225}$$

The same wave equation is satisfied by the pressure so that the above waves can also be seen as waves of pressure and they are nothing but the sound waves in the fluid. The resulting behavior of ρ and $\boldsymbol{v}$ is not relaxation to equilibrium but rather oscillating behavior corresponding to sound.

It is important to be aware of the meaning of the difference of the above expression for c_s from the expression derived by Newton. Newton considered sound as an essentially mechanistic phenomenon, assuming that sound propagates at a constant temperature in the fluid which gives $c_s^2 = (\partial p / \partial \rho)_T$. Laplace corrected this result by noting that it is the transfer of heat that does not have enough time to occur during the wave propagation rather than the exchange of temperature. As a result of this difference it seems very hard (if not impossible) to derive a mechanical model for sound that would produce the correct propagation speed.

Thus in the considered order of the expansion in k, the equations are not dissipative. In other words, the first order terms in the Taylor expansion of $\lambda_{ij}(\boldsymbol{k})$ at $k = 0$ give zero contribution into the decay rates of perturbations. The leading order at small k contribution to the decay rates comes only from the second order terms in the Taylor expansion, to the study of which we pass now.

B. Linearized equations of hydrodynamics to second order in derivatives. Normal relaxation modes in a fluid.

We consider the equations that correspond to keeping in the Taylor expansion of $\lambda_{ij}(\boldsymbol{k})$ the terms which are quadratic in k that is we consider the approximation $\lambda_{ij}(\boldsymbol{k}) \approx C_{ijl} k_l + M_{ijmn} k_m k_n / 2$, where $M_{ijmn} = \partial_m \partial_n \lambda_{ij}(k = 0)$. Again it is more convenient to consider the equations in the real space. In this order the equations correspond to adding to Eqs. (221) for τ_{ij} and $\boldsymbol{j}^E$ some additional terms linear in the derivatives of the fields. Gradients of thermodynamic variables do not produce a macroscopic flux of momentum (for example steady states of fluids with imposed gradients of temperature do not involve a macroscopic flow) so the additional contribution to τ_{ij} contains only the gradients of velocity. This contribution describes the friction force between the nearby layers of the fluid at relative motion. The most general form allowed by the isotropy, the parity and the symmetry of τ_{ij} is

$$\tau_{ij} = p\delta_{ij} - \eta \left[\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} - \frac{2}{3} \delta_{ij} \nabla \cdot \boldsymbol{v} \right] - \zeta \delta_{ij} \nabla \cdot \boldsymbol{v}, \tag{226}$$

where the traceless part of the tensor of velocity derivatives has been singled out as the $\eta-$term. The coefficients η and ζ are called shear and bulk viscosities respectively. The corresponding addition to the energy flux is

$$\boldsymbol{j}^E = (\rho\epsilon + p)\boldsymbol{v} - \kappa\nabla T, \tag{227}$$

where the additional contribution describes the heat flux and it corresponds to the so-called Fick's law. The coefficient κ is called the heat conductivity. The term containing ∇p, that could in principle be added to $\boldsymbol{j}^E$, can be shown to be forbidden by the Onsager symmetry relation. We obtain the following system of the so-called linearized equations of hydrodynamics:

$$\frac{\partial \rho}{\partial t} = -\rho_0 \nabla \cdot \boldsymbol{v}, \quad \rho_0 \frac{\partial \boldsymbol{v}}{\partial t} = -\nabla p + \eta \nabla^2 \boldsymbol{v} + \left(\frac{\eta}{3} + \zeta \right) \nabla(\nabla \cdot \boldsymbol{v}), \quad \rho_0 \frac{\partial \epsilon}{\partial t} + \epsilon_0 \frac{\partial \rho}{\partial t} = -(\rho_0 \epsilon_0 + p_0)\nabla \cdot \boldsymbol{v} + \kappa \nabla^2 T \tag{228}$$

Note that in general η, ζ and κ are functions of the local thermodynamic variables but in the considered order of approximation they can be substituted by their constant value in equilibrium. With the addition of the second derivative terms into the equations, the entropy is no longer conserved - Eq. (222) is modified to

$$\rho_0 T_0 \frac{\partial s}{\partial t} = \kappa \nabla^2 T. \tag{229}$$

As a result, there is dissipation and the equations (228) describe relaxation to equilibrium. For the analysis it is convenient to choose s and p as two independent thermodynamic variables. The equations (228) become

$$\left(\frac{\partial \rho}{\partial s} \right)_p \frac{\partial s}{\partial t} + \left(\frac{\partial \rho}{\partial p} \right)_s \frac{\partial p}{\partial t} = -\rho_0 \nabla \cdot \boldsymbol{v}, \quad \rho_0 \frac{\partial \boldsymbol{v}}{\partial t} = -\nabla p + \eta \nabla^2 \boldsymbol{v} + \left(\frac{\eta}{3} + \zeta \right) \nabla(\nabla \cdot \boldsymbol{v}),$$

$$\rho_0 T_0 \frac{\partial s}{\partial t} = \kappa \left(\frac{\partial T}{\partial s} \right)_p \nabla^2 s + \kappa \left(\frac{\partial T}{\partial p} \right)_s \nabla^2 p. \tag{230}$$

We look for the normal modes of the above system in the standard form

$$P(\boldsymbol{r}, t) = P(\boldsymbol{k}, \omega)e^{i(\boldsymbol{k} \cdot \boldsymbol{r} - \omega t)}, \quad s(\boldsymbol{r}, t) = s(\boldsymbol{k}, \omega)e^{i(\boldsymbol{k} \cdot \boldsymbol{r} - \omega t)}, \quad \boldsymbol{v}(\boldsymbol{r}, t) = \boldsymbol{v}(\boldsymbol{k}, \omega)e^{i(\boldsymbol{k} \cdot \boldsymbol{r} - \omega t)}. \tag{231}$$

The amplitudes obey the system of equations

$$\omega\left(\frac{\partial\rho}{\partial s}\right)_p s(\boldsymbol{k},\omega) + \omega\left(\frac{\partial\rho}{\partial p}\right)_s p(\boldsymbol{k},\omega) - \rho_0\boldsymbol{k}\cdot\boldsymbol{v}(\boldsymbol{k},\omega) = 0, \quad \rho_0\omega\boldsymbol{v}(\boldsymbol{k},\omega) - \boldsymbol{k}p(\boldsymbol{k},\omega) = -ik^2\eta\boldsymbol{v}(\boldsymbol{k},\omega) - i\left(\frac{\eta}{3}+\zeta\right)$$

$$\times\boldsymbol{k}[\boldsymbol{k}\cdot\boldsymbol{v}(\boldsymbol{k},\omega)], \quad \rho_0 T_0\omega s(\boldsymbol{k},\omega) = -i\kappa\left(\frac{\partial T}{\partial s}\right)_p k^2 s(\boldsymbol{k},\omega) - i\kappa\left(\frac{\partial T}{\partial p}\right)_s k^2 p(\boldsymbol{k},\omega). \tag{232}$$

A remarkable property of the system above is that the transversal component of velocity $\boldsymbol{v}_t(\boldsymbol{k},\omega)$ decouples. The transversal component is defined by decomposing $\boldsymbol{v}(\boldsymbol{k},\omega)$ into a sum of a longitudinal component along $\boldsymbol{k}$ and a transversal component perpendicular to $\boldsymbol{k}$,

$$\boldsymbol{v}(\boldsymbol{k},\omega) = \boldsymbol{v}_l(\boldsymbol{k},\omega) + \boldsymbol{v}_t(\boldsymbol{k},\omega), \quad \boldsymbol{k}\times\boldsymbol{v}_l(\boldsymbol{k},\omega) = 0, \quad \boldsymbol{k}\cdot\boldsymbol{v}_t(\boldsymbol{k},\omega) = 0. \tag{233}$$

Then the system (232) gives

$$(\rho_0\omega + ik^2\eta)\boldsymbol{v}_t(\boldsymbol{k},\omega) = 0. \tag{234}$$

It follows that the dispersion relation for the transversal velocity modes (also called shear modes) is $\omega = -i\eta k^2/\rho_0$. There are two such modes that correspond to two possible directions of polarization. Putting the expression for ω into the definition provided by Eq. (231) we see that the perturbations of the transversal velocity decay diffusively with the diffusion coefficient proportional to η. Below we will use this to derive the Kubo formula for the viscosity coefficient.

The equations on s, p and v_l form a coupled system of three equations,

$$\omega\left(\frac{\partial\rho}{\partial s}\right)_p s(\boldsymbol{k},\omega) + \omega\left(\frac{\partial\rho}{\partial p}\right)_s p(\boldsymbol{k},\omega) - \rho_0 k v_l(\boldsymbol{k},\omega) = 0, \quad -kp(\boldsymbol{k},\omega) + \left[\rho_0\omega + ik^2\left(\frac{4\eta}{3}+\zeta\right)\right]v_l(\boldsymbol{k},\omega) = 0,$$

$$\left[\omega + ik^2\frac{\kappa}{\rho_0 T_0}\left(\frac{\partial T}{\partial s}\right)_p\right]s(\boldsymbol{k},\omega) + ik^2\frac{\kappa}{\rho_0 T_0}\left(\frac{\partial T}{\partial p}\right)_s p(\boldsymbol{k},\omega) = 0. \tag{235}$$

The system has the form $M_{ij}(k,\omega)x_j = 0$ where $\boldsymbol{x} = [\rho(\boldsymbol{k},\omega), v_l(\boldsymbol{k},\omega), p(\boldsymbol{k},\omega)]$. The dispersion relation $\omega = \omega(k)$ is fixed by the demand that the system has non-trivial solutions, that is $\det M(k,\omega) = 0$. The explicit form of the last condition is

$$\left[\omega^2 - k^2\left(\frac{\partial p}{\partial\rho}\right)_s + i\frac{\omega k^2}{\rho_0}\left(\frac{4\eta}{3}+\zeta\right)\right]\left[\omega + ik^2\frac{\kappa}{\rho_0 T_0}\left(\frac{\partial T}{\partial s}\right)_p\right] - i\omega k^2\frac{\kappa}{\rho_0 T_0}\left(\frac{\partial T}{\partial p}\right)_s\left(\frac{\partial\rho}{\partial s}\right)_p\left(\frac{\partial p}{\partial\rho}\right)_s$$

$$\times\left[\omega + i\frac{k^2}{\rho_0}\left(\frac{4\eta}{3}+\zeta\right)\right] = 0. \tag{236}$$

Using the definitions $c_p = T_0(\partial s/\partial T)_p$ and $c_p = T_0(\partial s/\partial T)_\rho$, where c_p and c_v are the heat capacities per particle, and the identity

$$\left(\frac{\partial T}{\partial p}\right)_s\left(\frac{\partial\rho}{\partial s}\right)_p\left(\frac{\partial p}{\partial\rho}\right)_s = \left(\frac{\partial T}{\partial s}\right)_p - \left(\frac{\partial T}{\partial s}\right)_\rho = -T_0\left(\frac{1}{c_v} - \frac{1}{c_p}\right), \tag{237}$$

we may rewrite Eq. (236) as

$$\left(\omega + ik^2\frac{\kappa}{\rho_0 c_p}\right)\left[\omega^2 - k^2 c_s^2 + i\omega\frac{k^2}{\rho_0}\left(\frac{4\eta}{3}+\zeta+\kappa\left[\frac{1}{c_v}-\frac{1}{c_p}\right]\right)\right] - \frac{\omega k^4\kappa}{\rho_0}\left(\frac{1}{c_v}-\frac{1}{c_p}\right)\left(\frac{4\eta}{3}+\zeta-\frac{\kappa}{c_p}\right) = 0, \tag{238}$$

where c_s is the speed of sound as defined by Eq. (225). The dispersion relation $\omega = \omega(k)$ obtained from the equation above can only be correct up to the terms of order k^2 - a meaningful answer for higher order terms would demand the account of higher order terms in $\lambda_{ij}(\boldsymbol{k})$ in the original system of the equations. Solving Eq. (238) to order k^2 we find three solutions,

$$\omega_1(k) = -i\frac{\kappa k^2}{\rho_0 c_p}, \quad \omega_\pm(k) = \pm c_s k - i\Gamma k^2, \tag{239}$$

where the sound absorption coefficient Γ is defined by

$$\Gamma = \frac{1}{2\rho_0}\left(\frac{4\eta}{3} + \zeta + \kappa\left[\frac{1}{c_v} - \frac{1}{c_p}\right]\right). \tag{240}$$

The mode corresponding to ω_1 is a purely diffusive mode. Considering the corresponding eigenvector one finds that its components satisfy the following scaling in k,

$$s[\boldsymbol{k}, \omega_1(k)] \propto 1, \quad v_l[\boldsymbol{k}, \omega_1(k)] \propto k, \quad p[\boldsymbol{k}, \omega_1(k)] \propto k^2. \tag{241}$$

Since we work in the regime of small k it follows that this mode is composed predominantly of the fluctuations of entropy which decay exponentially like in diffusion. This mode corresponds to the propagation of heat and it is sometimes called the heat mode or the entropy mode. The eigenvector that corresponds to $\omega_\pm$ satisfies the following scaling

$$v_l[\boldsymbol{k}, \omega_1(k)] \propto p[\boldsymbol{k}, \omega_1(k)] \propto 1, \quad s[\boldsymbol{k}, \omega_1(k)] \propto k. \tag{242}$$

Thus these modes correspond predominantly to a pressure wave. These are longitudinal sound waves with real part of $\omega_\pm(k)$ describing the wave propagation in the two possible directions and the imaginary part of $\omega_\pm(k)$ describing slow exponential decay of the amplitude of the propagating wave (the slowness is a consequence of $|Im\ \omega_\pm(k)| \ll |Re\ \omega_\pm(k)|$).

Thus in the hydrodynamic regime there are five channels of relaxation in normal fluids that correspond to two shear modes, two sound modes and one heat mode.

C. Calculation of the dynamical structure factor

To be introduced

D. The Kubo formula for viscosity

We have seen in the example of the spin diffusion that one can derive the Kubo formula for the diffusion coefficient by representing the latter in terms of the spectrum of fluctuations of magnetization and then reexpressing the result in terms of the spectrum of the fluctuations of the current. Diffusion coefficient describes dissipation of perturbations so that the obtained expression is an example of the fluctuation-dissipation theorem. In fluids there are 3 coefficients that describe dissipation: shear viscosity η determines the decay of the shear modes, heat conductivity κ determines the decay of the heat mode and Γ determines the decay of sound modes. Equivalently, one can say that η, κ and ζ are dissipation coefficients, and expect that a corresponding Kubo formula holds for them. Here we give the formula for η which derivation is somewhat simpler. Taking the curl of the velocity equation in Eqs. (228) we have

$$\rho_0 \frac{\partial \boldsymbol{\omega}}{\partial t} = \eta \nabla^2 \boldsymbol{\omega}, \tag{243}$$

where $\boldsymbol{\omega} \equiv \nabla \times \boldsymbol{v}$ is the so-called vorticity field. Vorticity is very important in non-linear hydrodynamics and its dynamics plays crucial role in such ill-understood phenomena as tornados. Within the linearized hydrodynamics, however, vorticity obeys a simple diffusion equation with diffusion coefficient determined by the shear viscosity. Thus we may derive the Kubo formula for η following exactly the same lines as we did for the spin diffusion coefficient. For the derivation it is more convenient not to use the vorticity but rather the transversal component of velocity. Taking Fourier transform of the velocity equation in Eqs. (228) we find

$$\rho_0 \frac{\partial \boldsymbol{v}(\boldsymbol{k}, t)}{\partial t} = -i\boldsymbol{k}p(\boldsymbol{k}, t) - \eta k^2 \boldsymbol{v}(\boldsymbol{k}, t) - \left(\frac{\eta}{3} + \zeta\right)\boldsymbol{k}\left[\boldsymbol{k} \cdot \boldsymbol{v}(\boldsymbol{k}, t)\right] \tag{244}$$

The above equation holds for any $\boldsymbol{k}$. Let us choose $\boldsymbol{k}$ in x−direction, $\boldsymbol{k} = k\hat{x}$, and consider the y component of the equation. We find

$$\rho_0 \frac{\partial v_y(k\hat{x}, t)}{\partial t} = -\eta k^2 v_y(k\hat{x}, t). \tag{245}$$

The above equation expresses the decoupling of the transversal component of velocity which obeys simple diffusion equation. Using the Onsager hypothesis we may write immediately that

$$\langle v_y(k\hat{x}, t)v_y(-k\hat{x}, 0)\rangle = \langle v_y(k\hat{x}, 0)v_y(-k\hat{x}, 0)\rangle \exp\left[-\frac{\eta k^2|t|}{\rho_0}\right]. \tag{246}$$

It follows that the function $S(k, \omega)$ defined by

$$S(k, \omega) = \int e^{i\omega t}\langle v_y(k\hat{x}, t)v_y(-k\hat{x}, 0)\rangle dt, \tag{247}$$

is given by

$$S(k, \omega) = \langle v_y(k\hat{x}, 0)v_y(-k\hat{x}, 0)\rangle \frac{2(\eta k^2/\rho_0)}{(\eta k^2/\rho_0)^2 + \omega^2}. \tag{248}$$

Next we note that the $y-$ component of the momentum conservation equation, which to lowest order reads $\rho_0\partial_t v_y = -\partial_j \tau_{yj}$, gives after Fourier transform over both space and time that

$$\tau_{yx}(k\hat{x}, \omega) = -\frac{\rho_0\omega v_y(k\hat{x}, \omega)}{k}, \tag{249}$$

where for the wavenumber we set $\boldsymbol{k} = k\hat{x}$. Using the above equation, we find that $\tilde{S}(k, \omega)$ defined by

$$\tilde{S}(k, \omega) = \int e^{i\omega t}\langle \tau_{yx}(k\hat{x}, t)\tau_{yx}(-k\hat{x}, 0)\rangle dt, \tag{250}$$

obeys

$$\tilde{S}(k, \omega) = \frac{\rho_0^2\omega^2}{k^2}S(k, \omega) = \langle v_y(k\hat{x}, 0)v_y(-k\hat{x}, 0)\rangle \frac{2\eta\rho_0\omega^2}{(\eta k^2/\rho_0)^2 + \omega^2}. \tag{251}$$

where we used Eq. (248). The above equation implies that

$$\lim_{\omega\to 0}\lim_{k\to 0}\tilde{S}(k, \omega) = 2\eta\rho_0\lim_{k\to 0}\langle v_y(k\hat{x}, 0)v_y(-k\hat{x}, 0)\rangle. \tag{252}$$

Using the definition (250) and Eq. (213) we have from the above equation that

$$2\eta\rho_0\lim_{k\to 0}\langle v_y(k\hat{x}, 0)v_y(-k\hat{x}, 0)\rangle = \lim_{\omega\to 0}\lim_{k\to 0}V\int dtd\boldsymbol{r}e^{i\omega t - ikx}\langle \tau_{yx}(\boldsymbol{r}, t)\tau_{yx}(0, 0)\rangle. \tag{253}$$

We now calculate $\lim_{k\to 0}\langle v_y(k\hat{x})v_y(-k\hat{x})\rangle$. We have

$$\lim_{k\to 0}\langle v_y(k\hat{x})v_y(-k\hat{x})\rangle = \lim_{k\to 0}\int d\boldsymbol{r}d\boldsymbol{r}'\exp[-ik(x - x')]\langle v_y(\boldsymbol{x})v_y(\boldsymbol{x}')\rangle = V\int\langle v_y(\boldsymbol{r})v_y(0)\rangle d\boldsymbol{r}. \tag{254}$$

To fix the last integral we consider a macroscopic subsystem of the fluid which is much smaller than the whole system. We choose the subsystem size L to be much larger than the correlation length of velocity l_{cor} (so that $\langle v_y(\boldsymbol{r})v_y(0)\rangle$ is negligible at $r \gg l_{cor}$) and designate the subsystem volume by Ω. We now ask what is the probability distribution of the center of mass velocity $\boldsymbol{V}$ of the considered volume. Neglecting the energy of interaction of the subsystem with its exterior (which means neglecting surface effects against the volume ones) we have that the fluid energy is the sum of the energies of the subsystem and its environment. Representing the former energy as the sum of the center of mass energy and the internal energy we find that the distribution of $\boldsymbol{V}$ is determined by the Boltzmann factor,

$$P(\boldsymbol{V}) \propto \exp\left[-\frac{MV^2}{2k_BT}\right], \tag{255}$$

where $M = \rho_0\Omega$ is the mass of the subsystem. Here one needs not account for the fluctuations of M in the leading order of consideration of small fluctuations. Note that the above formula is valid also within the frame of the quantum mechanical consideration as center of mass is a quasi-classical variable. It follows from the above that

$$\langle V^2\rangle = \frac{3k_BT}{M} = \frac{3k_BT}{\rho_0\Omega}. \tag{256}$$

On the other hand we may represent the above average with the help of the velocity field as

$$\langle V^2 \rangle = \langle \left[\int_\Omega \frac{d\boldsymbol{r}}{\Omega} v(\boldsymbol{r}) \right]^2 \rangle = \frac{1}{\Omega^2} \int d\boldsymbol{r} d\boldsymbol{r}' \langle v_i(\boldsymbol{r}) v_i(\boldsymbol{r}') \rangle \approx \frac{1}{\Omega} \int \langle v_i(\boldsymbol{r}) v_i(0) \rangle d\boldsymbol{r}, \tag{257}$$

where in the last equation we used $L \gg l_{cor}$. Comparing the last two equations we find

$$\int \langle v_i(\boldsymbol{r}) v_i(0) \rangle d\boldsymbol{r} = \frac{3 k_B T}{\rho_0}. \tag{258}$$

Since by isotropy all three components of v_i give equal contribution into the above equation, we obtain

$$\int \langle v_y(\boldsymbol{r}) v_y(0) \rangle d\boldsymbol{r} = \frac{k_B T}{\rho_0}, \quad \lim_{k \to 0} \langle v_y(k\hat{x}) v_y(-k\hat{x}) \rangle = \frac{k_B T V}{\rho_0}. \tag{259}$$

Putting the above into Eq. (253) we find

$$\eta = \lim_{\omega \to 0} \lim_{k \to 0} \frac{1}{2 k_B T} \int dt d\boldsymbol{r} e^{i\omega t - ikx} \langle \tau_{yx}(\boldsymbol{r}, t) \tau_{yx}(0, 0) \rangle. \tag{260}$$

Finally, performing the symmetrization of the current like we did in the analysis of the spin diffusion coefficient we find the Kubo formula for viscosity

$$\eta = \lim_{\omega \to 0} \lim_{k \to 0} \frac{1}{4 k_B T} \int dt d\boldsymbol{r} e^{i\omega t - ikx} \langle [\tau_{yx}(\boldsymbol{r}, t), \tau_{yx}(0, 0)]_s \rangle. \tag{261}$$

The above formula is used a lot today as it turned out that the shear viscosity η is a rather basic object to calculate in quantum field theories with gravity duals (i. e. theories allowing isomorphism to a certain theory of spacetime).

It is possible to derive Kubo formulas for κ and ζ as well. Here we bring the formula for ζ. Both η and ζ describe the transport of momentum and the general formula reads

$$\eta \left(\delta_{ij} + \frac{1}{3} \frac{k_i k_j}{k^2} \right) + \zeta \frac{k_i k_j}{k^2} == \lim_{\omega \to 0} \lim_{k \to 0} \frac{1}{4 k_B T} \int dt d\boldsymbol{r} e^{i\omega t - i\boldsymbol{k} \cdot \boldsymbol{r}} \sum_{m,n} \frac{k_m k_n}{k^2} \langle [\tau_{im}(\boldsymbol{r}, t), \tau_{jn}(0, 0)]_s \rangle. \tag{262}$$

The result (261) is obtained by putting in the above equation $\boldsymbol{k} = k\hat{x}$ and $i = j = y$.

VII. NON-LINEAR LANGEVIN EQUATION AND FOKKER-PLANCK EQUATION

Today's understanding of complex, macroscopic systems has a clear dichotomy into near equilibrium and far from equilibrium situations. In equilibrium, considered systems find themselves in a statistically steady state described by a known probability distribution function. The problem of predicting the properties of a system in equilibrium is then facilitated (though by no means solved) by the knowledge of the distribution. Near equilibrium situations allow similar simplifications. In sharp contrast, understanding of systems far from equilibrium, which includes an important class of open, living systems, is very modest. An important class of situations where one can anticipate some advancement in understanding are non-equilibrium steady states. Here the probability distribution is not known and there are no general principles allowing to fix it. Often one resorts to modeling the system by some effective dynamics...

The general Langevin equation on an $n-$dimensional vector $x_i(t)$ reads

$$\frac{dx_i}{dt} = h_i(\boldsymbol{x}(t), t) + g_{ij}(\boldsymbol{x}(t), t) \Gamma_j(t), \tag{263}$$

where the Gaussian noise $\Gamma_i(t)$ is determined by $\langle \Gamma \rangle = 0$ and $\langle \Gamma_i(t) \Gamma_j(t') \rangle = 2 \delta_{ij} \delta(t - t')$. Let us stress that x_i above can have any meaning and though we use the same notation as for the spatial coordinate, it must be clear from the context, which one is meant (for example x_i above may well represent the velocity $\boldsymbol{v}$ of a Brownian particle).

It is natural to try to think of the equation (263) by seeing the evolution of $\boldsymbol{x}$ as composed of local drift caused by $\boldsymbol{h}$ and the local diffusion described by g_{ij}. This separation however is not precisely true. The equation (263) involves a singular term $\Gamma(t)$ and as such it determines the evolution of $\boldsymbol{x}(t)$ incompletely - one has to supply a *regularization* that explains how to understand $\Gamma(t)$ in the case where there is an ambiguity. To explain the problem, let us average Eq. (263) to obtain the equation on the evolution of the first moment of $\boldsymbol{x}(t)$,

$$\frac{d\langle x_i \rangle}{dt} = \langle h_i(\boldsymbol{x}(t), t) \rangle + \langle g_{ij}(\boldsymbol{x}(t), t) \Gamma_j(t) \rangle. \tag{264}$$

It is tempting to put the last term equal to zero. In fact, this would be wrong generally. Consider $\Gamma(t)$ within the framework of the so-called physical regularization, where it is recognized that in reality all processes have a finite correlation time and the Langevin equation is an effective description of the situation where the correlation time of Γ is much less than all other characteristic times in the problem. Then $g_{ij}(\boldsymbol{x}(t), t)$ is determined by $\Gamma(t')$ with $t' < t$ and it is correlated with $\Gamma(t)$ because $\Gamma(t')$ with $t' < t$ are correlated with it. As a result, within the physical regularization $\langle g_{ij}(\boldsymbol{x}(t), t)\Gamma_j(t)\rangle \neq 0$ and the diffusion leads to the variable drift additional to the one caused by $\boldsymbol{h}$. We will find this additional drift below.

Other popular ways of regularization used in the so-called stochastic calculus are Ito and Stratanovich ones. In particular, in the former one $\langle g_{ij}(\boldsymbol{x}(t), t)\Gamma_j(t)\rangle = 0$. The distinction between different ways of regularization is not important for the linear Langevin equation.

The non-linear Langevin equation is an example of the so-called Markov process. Markovian property is an important notion that appears in many applications, so it will be considered separately.

A. Markov processes

Probably the main property of Markov processes that makes them an important model is that they can be described as *evolution*, that is knowledge of statistics at any moment of time allows in principle to discuss the calculation of the statistics at later moments of time, without referring to the history of the process. A simplest example of such evolution problem is provided by the Fokker-Planck equation.

B. The Fokker-Planck equation

For non-linear Langevin equation (263) one can derive an explicit closed equation describing the evolution of probability densities in time. The equation is called the Fokker-Planck equation after the two people who first derived, independently, the equation on the distribution function for the Brownian motion.

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x_i}\left[D_i(\boldsymbol{x}, t)P(\boldsymbol{x}, t)\right] + \frac{\partial^2}{\partial x_i \partial x_j}\left[D_{ij}(\boldsymbol{x}, t)P(\boldsymbol{x}, t)\right], \tag{265}$$

where the so-called drift coefficient $D_i(\boldsymbol{x}, t)$ and the diffusion matrix $D_{ij}(\boldsymbol{x}, t)$ are defined by

$$D_i(\boldsymbol{x}, t) = h_i(\boldsymbol{x}, t) + g_{mj}(\boldsymbol{x}, t)\frac{\partial g_{ij}(\boldsymbol{x}, t)}{\partial x_m}, \quad D_{ij}(\boldsymbol{x}, t) = g_{im}(\boldsymbol{x}, t)g_{jm}(\boldsymbol{x}, t). \tag{266}$$

Note that the real eigenvalues of D_{ij} are never negative. They are strictly positive at points $\boldsymbol{x}$ where the matrix $g_{ij}(\boldsymbol{x}, t)$ is not degenerate. In the one-dimensional case the diffusion coefficient is simply $g^2(x, t)$.

It should be stressed that while the non-linear Langevin equation (263) contains ambiguity demanding for the completion of the definition, the PDF $P(\boldsymbol{x}, t)$ entering the Fokker-Planck equation is already a perfectly well-defined object. In particular, to pass from Langevin equation in one regularization to its counterpart in another representation one can compare the Fokker-Planck equations resulting in these representations. From now on we shall confine ourselves to the case of stationary Langevin dynamics, where the functions h_i and g_{ij} in Eq. (263) do not depend on time explicitly $h_i = h_i(\boldsymbol{x})$, $g_{ij} = g_{ij}(\boldsymbol{x})$. Let us consider some simple examples of the use of Eq. (265).

C. Some examples of the use of the Fokker-Planck equation

Brownian motion, FDT, Brownian motion in external potential

Now let us consider the equation of the Brownian motion including the coordinate into consideration,

$$\frac{d\boldsymbol{x}}{dt} = \boldsymbol{v}, \quad \frac{d\boldsymbol{v}}{dt} = -\frac{\boldsymbol{v}}{\tau} + C\boldsymbol{\Gamma}, \tag{267}$$

where C is determined from the FDT. The above equation is a Langevin of the general type (263) and we may write a Fokker-Planck equation for the PDF $P(\boldsymbol{x}, \boldsymbol{v}, t)$. We find

$$\frac{\partial P}{\partial t} + \boldsymbol{v}\nabla_{\boldsymbol{x}}P = \frac{\partial}{\partial v_i}\left[\frac{v_i}{\tau} + \frac{k_B T}{M\tau}\frac{\partial}{\partial v_i}\right]P. \tag{268}$$

We know that at times much larger than the correlation time τ of the velocity, the marginal distribution $P(\boldsymbol{x}, t) = \int P(\boldsymbol{x}, \boldsymbol{v}, t) d\boldsymbol{v}$, giving the PDF of $\boldsymbol{x}(t)$ must obey a simple diffusion equation. If we now integrate Eq. (268) over $\boldsymbol{v}$ we find that $P(\boldsymbol{x}, t)$ satisfies

$$\frac{\partial P(\boldsymbol{x}, t)}{\partial t} = -\frac{\partial}{\partial x_i} \langle v_i \rangle_{\boldsymbol{x}}, \tag{269}$$

where $\langle v_i \rangle_{\boldsymbol{x}} = \int v_i P(\boldsymbol{v}, \boldsymbol{x}, t) d\boldsymbol{v}$ is the "current" of $\boldsymbol{x}$. At $t \gg \tau$ one can show that $\langle v_i \rangle_{\boldsymbol{x}}$ obeys the "constitutive relation" $\langle v_i \rangle_{\boldsymbol{x}} = -D\nabla P$ leading to the diffusion equation $\partial_t P = D\nabla^2 P$ for $P(\boldsymbol{x}, t)$. To show the relation one can instead of taking the limit of large t at fixed τ, take the limit of small τ at fixed t. In this limit, one can drop $d\boldsymbol{v}/dt$ term in the second of Eqs. (267) which leads to $\dot{x}_i = \tau \Gamma_i$ producing the diffusion equation on $P(\boldsymbol{x}, t)$.

D. Some general properties of the Fokker-Planck equation

The Fokker-Planck equation has the form of a local conservation law

$$\frac{\partial P}{\partial t} + \nabla \cdot \boldsymbol{S} = 0, \tag{270}$$

where the probability current $\boldsymbol{S}$ is defined by

$$S_i = D_i P - \frac{\partial}{\partial x_j} [D_{ij} P]. \tag{271}$$

If the normal component of $\boldsymbol{S}$ vanishes at a boundary of some volume V then the probability $\int_V P(\boldsymbol{x}, t) d\boldsymbol{x}$ for $\boldsymbol{x}$ to be inside V is conserved. In particular, for the so-called natural boundary conditions, where the PDF and thus also the current vanish at infinity, the normalization of probability $\int P(\boldsymbol{x}, t) d\boldsymbol{x}$ is conserved in time. Consider now the evolution of the first moment of $\boldsymbol{x}(t)$,

$$\frac{d}{dt} \langle x_i(t) \rangle = \frac{\partial}{\partial t} \int x_i P(\boldsymbol{x}, t) d\boldsymbol{x} = \int d\boldsymbol{x} x_i \left[-\frac{\partial}{\partial x_j} (D_j P) + \frac{\partial^2}{\partial x_i \partial x_j} D_{ij} P \right]. \tag{272}$$

Assuming natural boundary conditions one can integrate by parts which leads to

$$\frac{d}{dt} \langle x_i(t) \rangle = \int D_i(\boldsymbol{x}) P(\boldsymbol{x}, t) d\boldsymbol{x} = \langle h_i[\boldsymbol{x}(t)] \rangle + \left\langle g_{mj}[\boldsymbol{x}(t)] \frac{\partial g_{ij}[\boldsymbol{x}(t)]}{\partial x_m} \right\rangle, \tag{273}$$

where we used the expression (266) for D_i. The above expression provides the explicit answer for the contact term in Eq. (??).

The Fokker-Planck equation is a linear equation so that the solution of the initial value problem can be written as

$$P(\boldsymbol{x}, t) = \int P(\boldsymbol{x}, \boldsymbol{x}', t) P(\boldsymbol{x}', t) d\boldsymbol{x}', \tag{274}$$

where the Green function $P(\boldsymbol{x}, \boldsymbol{x}', t)$ is defined as the solution of

$$\frac{\partial P(\boldsymbol{x}, \boldsymbol{x}', t)}{\partial t} = -\frac{\partial}{\partial x_i} [D_i(\boldsymbol{x}, t) P(\boldsymbol{x}, \boldsymbol{x}', t)] + \frac{\partial^2}{\partial x_i \partial x_j} [D_{ij}(\boldsymbol{x}, t) P(\boldsymbol{x}, \boldsymbol{x}', t)], \quad P(\boldsymbol{x}, \boldsymbol{x}', 0) = \delta(\boldsymbol{x} - \boldsymbol{x}'). \tag{275}$$

The distinguishing property of the Green function of the Fokker-Planck equation is that it is also the probability of the transition of the random process $\boldsymbol{x}(t)$ from $\boldsymbol{x}'$ to $\boldsymbol{x}$ in time t. In particular, if the diffusion matrix $D_{ij}(\boldsymbol{x})$ is non-degenerate everywhere then one can see that $P(\boldsymbol{x}, \boldsymbol{x}', t)$ is positive as one expects from the probability, see the section on the path integral representation of the solution.

E. The meaning of the drift coefficient and the diffusion matrix

To understand the meaning of the drift coefficient D_i and the diffusion matrix D_{ij} let us first consider the Fokker-Planck equation in the case where D_i and D_{ij} are constant,

$$\frac{\partial P}{\partial t} = -D_i \frac{\partial P}{x_i} + D_{ij} \frac{\partial^2 P}{\partial x_i \partial x_j}. \tag{276}$$

To find the Green function one notices that the above equation corresponds to the Langevin dynamics

$$\frac{dx_i}{dt} = D_i + g_{ij}\Gamma_j(t), \quad g_{ij}g_{kj} = D_{ij}, \quad \langle\Gamma\rangle = 0, \quad \langle\Gamma_i(t)\Gamma_j(t')\rangle = 2\delta_{ij}\delta(t-t'). \tag{277}$$

It follows from Gaussianity of Γ that $\boldsymbol{x} - \boldsymbol{x}(0) - \boldsymbol{D}t = \int_0^t g_{ij}\Gamma_j(t)$ is a Gaussian variable. This variable has zero mean and the pair correlation function

$$\langle[\boldsymbol{x} - \boldsymbol{x}(t=0) - \boldsymbol{D}t]_i[\boldsymbol{x} - \boldsymbol{x}(t=0) - \boldsymbol{D}t]_j\rangle = g_{ik}g_{jl}\int_0^t \Gamma_k(t_1)\Gamma_l(t_2) = 2g_{ik}g_{jk}t = 2D_{ij}t, \tag{278}$$

where we used Eq. (277). Thus under the condition $\boldsymbol{x}(0) = \boldsymbol{x}'$ the random variable $\boldsymbol{x}(t)$ is Gaussian with the mean $\langle x_i(t)\rangle = x_i'$ and the dispersion $\langle\langle x_i(t)x_j(t)\rangle\rangle = 2D_{ij}t$. The corresponding PDF of $\boldsymbol{x}(t)$, representing nothing but the Green function $P(\boldsymbol{x}, \boldsymbol{x}', t)$ of Eq. (276), is given by

$$P(\boldsymbol{x}, \boldsymbol{x}', t) = \frac{1}{(4\pi t)^{n/2}\sqrt{\det D}} \exp\left[-\frac{[\boldsymbol{x} - \boldsymbol{x}' - \boldsymbol{D}t]_i[\boldsymbol{x} - \boldsymbol{x}' - \boldsymbol{D}t]_j}{4t}D_{ij}^{-1}\right]. \tag{279}$$

The usefulness of the solution above is that it allows to see the form of the solution of the general Fokker-Planck equation for small times τ. To see this consider the evolution of $P(\boldsymbol{x}, \boldsymbol{x}', \tau)$ from its initial value $\delta(\boldsymbol{x} - \boldsymbol{x}')$.

This is why the Fokker-Planck equation is sometimes called a generalized diffusion equation.

F.   The functional integral representation of the solution

G.   One-dimensional Fokker-Planck equation

The Fokker-Planck equation in one dimension,

$$\frac{\partial P}{\partial t} = -\frac{\partial(D^1 P)}{\partial x} + \frac{\partial^2 P}{\partial x^2}, \tag{280}$$

has special properties that allow to reach much understanding of the solution. F

H.   Passage from the Schrodinger to the Fokker-Planck equation. Nelson formulation of the quantum mechanics.

We consider a quantum system consisting of N particles. Forming a $3N-$dimensional vector $\boldsymbol{x} = (\boldsymbol{x}_1, \boldsymbol{x}_2, .., \boldsymbol{x}_N)$ the Hamiltonian operator can be written as

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla_x^2 + U(\boldsymbol{x}), \tag{281}$$

where $U(\boldsymbol{x})$ is the potential energy. The imaginary time Schrodinger equation is

$$-\frac{\partial\psi}{\partial t} = \hat{H}\psi. \tag{282}$$

We assume that the Hamiltonian is bounded from below and designate the energy and the wavefunction of the ground state by E_0 and ψ_0 respectively,

$$- \tag{283}$$

the zero of energy is chosen so that the ground state

I. Covariant formulation of the Fokker-Planck equation and passage to a constant diffusion coefficient

The problem of finding a solution to Hamiltonian dynamics is to large extent the problem of finding the correct coordinates to describe the problem. In classical mechanics these are action-angle coordinates, in quantum mechanics we look for coordinates in Hilbert space in which the Hamiltonian operator is diagonal. Analogously one may search for the best coordinates to describe the Langevin dynamics (263). In one-dimensional case, one can always pass to coordinates in the "phase space" where the diffusion coefficient becomes an arbitrary, coordinate independent constant. The qualitative arguments is simple" dividing Eq. (263) by g we get

$$\frac{1}{g(x)}\frac{dx}{dt} = \frac{h(x)}{g(x)} + \Gamma. \tag{284}$$

Assuming that the diffusion is not degenerate so that $D(x) = g^2(x)$ is everywhere positive, we may pass to a new variable $y(x)$ obeying $y'(x) = 1/g(x)$ and the above equation takes the form

$$\frac{dy}{dt} = \frac{h[x(y)]}{g[x(y)]} + \Gamma. \tag{285}$$

The Fokker-Planck equation satisfied by y already corresponds to the constant diffusion coefficient equal to one, which is seemingly given by

$$\frac{\partial P(y,t)}{\partial t} + \frac{\partial}{\partial y}\left[\frac{h[x(y)]}{g[x(y)]}P(y,t)\right] + \frac{\partial^2 P(y,t)}{\partial y^2}. \tag{286}$$

Now the above derivation is correct only qualitatively, but not quantitatively. The reason is that Eq. (263) is a stochastic differential equation and, as we mentioned, its complete definition involves also a regularization prescription. As a result the procedure of naive division of the equation is not correct - Eq. (285) is already not sensitive to the regularization, so necessarily we missed something on the way. To find the correct form of the Fokker-Planck equation on $P(y,t)$ we recall that the PDF $P(x,t)$ appearing in the Fokker-Planck equation is a perfectly well-defined object. Then the equation on $P_y(y,t)$ with $y' = 1/g$ can be obtained from the law of transformation of probability densities, $P(x)dx = P_y(y)dy$ or $P(x,t) = P_y[y(x),t]/g(x)$ and the Fokker-Planck equation on $P(x,t)$. We find

It follows that the naive division procedure miscalculates the drift. The correct Langevin equation on y, corresponding to the Fokker-Planck equation above reads

Let us now ask whether oin the general $d-$dimensional case one can also choose coordinates so that the diffusion matrix simplifies to a constant one. Trying to apply the naive division argument, one fails: the division by g, here meaning the multiplication of Eq. (263) by the inverse matrix g^{-1}, produces

$$g_{ij}^{-1}\frac{dx_j}{dt} = g_{ij}^{-1}h_j + \Gamma_i. \tag{287}$$

Now generally it is not possible to represent the LHS as a time-derivative of some vector function $\boldsymbol{y}[\boldsymbol{x}]$:

$$\frac{dy_i[\boldsymbol{x}(t)]}{dt} = \frac{\partial y_i}{\partial x_j}\frac{dx_j}{dt}, \tag{288}$$

and the demand that the LHS of Eq. (??) can be written dy_i/dt leads to the equation

$$\frac{\partial y_i}{\partial x_j} = g_{ij}^{-1}. \tag{289}$$

It follows from the symmetry of the matrix of second derivatives of $\boldsymbol{y}$ that only if

$$\frac{\partial g_{ij}^{-1}}{\partial x_k} = \frac{g_{ik}^{-1}}{\partial x_j}. \tag{290}$$

is satisfied then one can expect the equality (289). The above equation is in fact also sufficient for the solvability of Eq. (289). Now in general the above condition is not satisfied and we should not expect a transformation to an equation with a constant diffusion matrix to be possible. Now, because our argument above is based on the incorrect procedure of naive multiplication of the original Eq. (263) by g^{-1}, then we should consider the above as merely a way to see cheaply what is to be expected. The correct way to deal with the question of when we can pass to a constant diffusion matrix by changing the coordinates involves the so-called covariant form of the Fokker-Planck equation.

INTRODUCE THE FOKKER-PLANCK OPERATOR

J. Covariant form of the Fokker-Planck equation

K. Connection between the Fokker-Planck and Schrodinger equations

We already mentioned that there is a close connection between Let us consider S

L. Nelson's formulation of quantum mechanics

The summit of the connection between the Fokker-Planck and Schrodinger equations is Nelson's formulation of quantum mechanics. Within this formulation the averages resulting from quantum evolution are given an equivalent representation in terms of a stochastic process. Note that effective stochasticity appears already in the classical mechanics and it does not demand quantum-mechanical notions. This led Nelson, who discovered the new formulation in 1966 to write that if quantum mechanics was discovered in this language the history of conceptual foundations of modern physics would be different. Indeed, the new formulation tries to explain the results of experiments traditionally explained with the help of quantum mechanics in classical terms.

The possibility to pass from the Schrodinger equation to the Fokker-Planck equation of a particular form, that was described above, means that mathematic

We provide the Nelson formulation for quantum mechanics of a single particle in one dimension. We use units where $\hbar$ and particle mass are equal to one. The Green function of the Schrodinger equation can be represented as a path integral,

$$G(x, x', t) = \int_{w(0)=x'}^{w(t)=x} Dw \exp\left(iS[w]\right), \quad S[w] = \int_0^t \left(\frac{\dot{w}^2}{2} - V[w]\right), \tag{291}$$

where $w(t)$ is the particle coordinate and $V(w)$ is the potential. Considering imaginary time continuation of the above quantity, one finds that $exp(iS[w])$ becomes $\exp(-S[w])$ and the resulting equation starts to have a form of averaging over different trajectories with trajectory probability weight given by $\exp(-S[w])$. It becomes natural to consider "statistical moments"

$$\langle w(t_1)..w(t_n)\rangle \equiv \frac{\int Dw w(t_1)..w(t_n) \exp(-S[w])}{\int Dw \exp(-S[w])}. \tag{292}$$

Assuming the ordering $t_k > t_{k-1}$ one can express the above average in terms of quantum mechanical expectation value as,

$$\langle w(t_1)..w(t_n)\rangle = < \psi_0|\hat{q} \exp[-(t_2 - t_1)H]\hat{q}.. \exp[-(t_n - t_{n-1})H]\hat{q}|\psi_0 >, \tag{293}$$

where $\hat{q}$ is the position operator, H is the Hamiltonian and $|\psi_0 >$ is the ground state wave function.

M. The entropy growth (H-theorem) for the Fokker-Planck equation

The second law of thermodynamics states that one can associate with a closed system an entropy function. The function grows as the system relaxes to equilibrium and attains its maximum in the equilibrium state. On the other hand, the Fokker-Planck equation, at least near equilibrium, describes correctly the relaxation dynamics of slow variables. Therefore it is natural to ask if the second law allows an explicit formulation within the frame of the equation. Such formulation does exist and it is called H-theorem after the first theorem of the kind that appeared in the context of the Boltzmann equation and will be considered later. Here the theorem is due to Lebowitz and Bergmann and Graham.

One considers two different solutions of the Fokker-Planck equation, W_1 and W_2, satisfying

$$\partial_t W_1 + \nabla \cdot (\boldsymbol{D}W_1) = \partial_i (D_{ij}\partial_j W_1), \quad \partial_t W_2 + \nabla \cdot (\boldsymbol{D}W_2) = \partial_i (D_{ij}\partial_j W_2) \tag{294}$$

It is assumed that the solutions may represent physical probability density functions that is they are non-negative and normalized, $\int W_i(\boldsymbol{x}, t)d\boldsymbol{x} = 1$. One defines "entropy" by

$$S(t) = - \int W_1 \ln \frac{W_1}{W_2} d\boldsymbol{x} = - \int [W_1 \ln W_1 - W_1 \ln W_2] \, d\boldsymbol{x}. \tag{295}$$

As we shall see the above definition produces a natural generalization for the entropy. Let us note that S is a non-positive function. Using $\int W_i(\boldsymbol{x}, t) d\boldsymbol{x} = 1$ we may rewrite S as

$$S = - \int \left[W_1 \ln \frac{W_1}{W_2} - W_1 + W_2 \right] d\boldsymbol{x} = - \int W_2 \left[R \ln R - R + 1 \right] d\boldsymbol{x}, \tag{296}$$

where we introduced $R \equiv W_1/W_2$. The last term in the above equation is always not positive as it follows from

$$R \ln R - R + 1 = \int_1^R \ln x \, dx \geq 0, \tag{297}$$

holding for any $R \geq 0$. Next we consider $\dot{S}$:

$$\dot{S} = \int \left[\ln \frac{W_1}{W_2} \nabla \cdot (\boldsymbol{D} W_1) - \frac{W_1}{W_2} \nabla \cdot (\boldsymbol{D} W_2) \right] d\boldsymbol{x} - \int \left[\ln \frac{W_1}{W_2} \partial_i (D_{ij} \partial_j W_1) - \frac{W_1}{W_2} \partial_i (D_{ij} \partial_j W_2) \right] d\boldsymbol{x}, \tag{298}$$

where we separated the derivative into the contribution of current and diffusion terms and used $\int \dot{W}_1(\boldsymbol{x}, t) d\boldsymbol{x} = 0$. Making the assumption that integration by parts is allowed (which here means that the current $\boldsymbol{D}$ is non-singular and it does not lead to run-away solutions of the "noiseless" Langevin equation $\dot{x} = \boldsymbol{D}[\boldsymbol{x}(t)]$), one finds that the contribution of the current terms vanishes. For the contribution of the diffusion term the integration by parts gives

$$\dot{S} = \int \left[D_{ij} \frac{\partial W_1}{\partial x_j} \frac{\partial}{\partial x_i} \left(\ln \frac{W_1}{W_2} \right) - D_{ij} \frac{\partial W_2}{\partial x_j} \frac{\partial}{\partial x_i} \left(\frac{W_1}{W_2} \right) \right] d\boldsymbol{x} = \int D_{ij} \frac{\partial}{\partial x_i} \left(\ln \frac{W_1}{W_2} \right) \left[\frac{\partial W_1}{\partial x_j} - \frac{W_1}{W_2} \frac{\partial W_2}{\partial x_j} \right]. \tag{299}$$

Introducing $\xi \equiv \ln(W_1/W_2)$ and assuming that the diffusion matrix is positive definite we find

$$\dot{S} = \int W_1 D_{ij} \frac{\partial \xi}{\partial x_i} \frac{\partial \xi}{\partial x_j} \geq 0, \tag{300}$$

where we equality occurs only if $W_1 = W_2$ (assuming $W_1 > 0$ everywhere). Note that in the above analysis the current $\boldsymbol{D}$ and the diffusion matrix D_{ij} may be the functions of both coordinate and time.

The integral in Eq. (300) determines a kind of a "distance" between W_1 and W_2 : it is always non-negative and it vanishes only if $W_1 = W_2$. Thus as long as $W_1 \neq W_2$, the entropy will grow. Since the entropy is bounded from above by zero, then, assuming $S(0)$ is finite, it is not possible that the distance between W_1 and W_2 remains above an arbitrary small $\epsilon > 0$ indefinitely. This implies that under the assumptions allowing the integration by parts in the above derivation, any two solutions of the Fokker-Planck equation will tend to agree at large times. In particular, if there is a stationary, normalizable solution P_{st} of the Fokker-Planck equation, then for any state of the system, as defined by the time-dependent probability density function P, one may introduce the entropy

$$S_0(t) = - \int P \ln \frac{P}{P_{st}} d\boldsymbol{x}. \tag{301}$$

Such entropy always increases reaching its absolute maximum in the "equilibrium" with $P = P_{st}$. This finishes establishing the form of the second law for the Fokker-Planck equation.

N. Examples of use of the entropy growth theorem

The entropy growth theorem allows one to deal with the problem of convergence to the stationary solution, when the latter exists, in situations where the Fokker-Planck equation does not have the special gradient form described by Eq. (**??**). It must be stressed that the gradient form does not hold already in the simplest situations, for example it does not hold for the Kramers equation (302) below. However, the theorem applies only if D_{ij} is a non-degenerate matrix, while in many situations it is in fact degenerate. A simple example is provided by the one-dimensional Kramers equation

$$\frac{\partial P(x, v, t)}{\partial t} = \left[- \frac{\partial}{\partial x} v + \frac{\partial}{\partial v} \left(\frac{v}{\tau} + \frac{1}{M} \frac{dU}{dx} \right) + \frac{k_B T}{M \tau} \frac{\partial}{\partial v^2} \right] P, \tag{302}$$

describing Brownian motion in an external potential U,

$$\frac{dx}{dt} = v, \quad \frac{dv}{dt} = - \frac{v}{\tau} - \frac{1}{M} \frac{dU}{dx} + \frac{f}{M}. \tag{303}$$

The above equation cannot be written in the gradient form while the diffusion matrix is degenerate with only one non-vanishing component D_{vv}. Thus while we know that the Boltzmann distribution $P_{eq}(x,v) = N\exp[-Mv^2/2k_BT - U(x)/k_BT]$ is a stationary solution of Eq. (302) the results shown before do not guarantee that an arbitrary initial state will relax to the Boltzmann distribution. Let us show how one can still use the entropy growth theorem to show that a general solution of the Kramers equation does converge to the Boltzmann distribution at large times. We note that Eq. (300) implies for Kramers equation that $\partial\xi/\partial v$ where $\xi = \ln W(x,v,t)/P_{eq}$ must tend to zero at large t for any solution W of the Fokker-Planck equation. This implies that at large times any distribution will take the form

$$W(x,v,t) = h(x,t)\exp\left[-\frac{MV^2}{2k_BT}\right], \tag{304}$$

where h is some function of x and t. Inserting the above into the Kramers equation (302) we find that h obeys

$$\frac{\partial h}{\partial t} = \left(-\frac{\partial}{\partial x} - \frac{1}{k_BT}\frac{dU}{dx}\right)vh. \tag{305}$$

Because h is independent of velocity v it follows that

$$\frac{\partial h}{\partial t} = 0, \quad h = h_o\exp\left[-\frac{U(x)}{k_BT}\right]. \tag{306}$$

Thus relying on the entropy growth theorem we were able to show that the stationary solution is also unique for the Kramers equation and all initial conditions relax to it at large times. It is important that we may actually demonstrate this result which is expected on physical grounds.

The usefulness of the entropy growth theorem is not limited to demonstrating uniqueness of the stationary solution and the convergence to it at large times. In particular, as we mentioned, the theorem holds even if the coefficients of the Fokker-Planck equation depend on time where there is no meaning to a stationary solution. An important case of problems with no stationary solution is diffusion-like problems. Consider one-dimensional diffusion equation

$$\frac{\partial P}{\partial t} = D\frac{\partial^2 P}{\partial x^2}. \tag{307}$$

If we consider diffusion on an infinite line then there is no stationary solution to the above equation - the particle diffuses spreading over a continuously growing region of space. It turns out that in this and many other similar situations the role of the stationary solution is played by a self-similar solution. The self-similar solution is a solution of the form $P(x,t) = t^{-\alpha}\Phi(x^\beta/t)$ where α and β are some constants and Φ is some function (due to the normalization condition $\int P(x,t)dx = 1$ one has $\alpha\beta = 1$). The evolution of such solution in time is dull - the plot of the function at a later time can be obtained from the previous one by a simple rescaling of the units on the axes. This "triviality" of the evolution is next in complexity after the stationary solution which is a particular case of a self-similar solution with unit rescaling. In particular, when a slef-similar solution ansatz is plugged in the Fokker-Planck equation, then, if such solution exists, it is found from ODE on Φ rather than the PDE. For diffusion equation the search for a self-similar solution leads to

$$P_s(x,t) = \frac{1}{\sqrt{4\pi Dt}}\exp\left[-\frac{x^2}{4Dt}\right]. \tag{308}$$

Of course $P_s(x,t) = G(x,x',t)$ where the Green function $G(x,x',t)$ solves Eq. (307) with the initial condition $G(x,x',0 = \delta(x-x')$. Now the H-theorem still says that any two solutions of the Fokker-Planck equation must converge at large times. Hence we conclude that at large times all solutions of the diffusion equation become approximately self-similar and are described by Eq. (308).

The above conclusion is easy to derive for the diffusion equation. First we note that $G(x,x',t)$ is just a shifted distribution $P_s(x,t)$ that is $G(x,x',t) = P_s(x-x',t)$. At large times where $\sqrt{DT} \gg x'$ we have $G(x,x',t) \approx G(x,0,t)$ which shows the conclusion of the theorem for the Green function solution of the Fokker-Planck equation. For arbitrary solution we have the general expression $P(x,t) = \int G(x,x',t)P(x',0)dx'$ and at times where $\sqrt{Dt}$ is much larger both than the center of mass x_c and the width of the initial distribution we have $P(x,t) \approx \int G(x,x_c,t)P(x',0)dx' = G(x,x_c,t)$. Thus we see that at large times $P(x,t)$ converges to $P_s(x,t)$. Of course to improve the rate of convergence it is better to use $G(x,x_c,t)$, which is just a shifted self-similar solution, instead of $G(x,0,t)$.

While for diffusion equation the above conclusions are rather easy to see directly, in more complicated situations the search for a self-similar solution and then the proof of the asymptotic convergence to it based on H-theorem constitute a very efficient way of deriving large-time behavior of the solutions.

VIII. BOLTZMANN EQUATION

Boltzmann equation is historically the first case when it became possible to see how microscopic laws give rise to macroscopic ones. The corresponding passage from one level of description (microscopic one) to another (macroscopic one) involves an assumption that cannot be derived on purely mechanical grounds. Thus Boltzmann equation has value additional to the merely practical one - it lays bare what is needed (in the case of the gas) in order to pass from the microscopic time-reversible dynamics to the irreversible macroscopic dynamics.

Physical systems that can be studied with the help of the Boltzmann equation are dilute gases of (quasi) particles. We consider ordinary molecular gases. If we designate the radius of molecular interactions by d then the condition that the gas is dilute is $\epsilon \equiv nd^3 \ll 1$ where n is the concentration of particles. Since the average distance $n^{-1/3}$ between the particles is much larger than their effective size d then most of the time each molecule moves freely. The dynamics of the gas is the free motion of particles interrupted by collisions between pairs of particles. The collisions, though rare, play crucial role in the gas relaxation to equilibrium - it is them which make the system dynamics chaotic allowing for mixing (forgetting of initial conditions and relaxation). Note that in the basic equilibrium statistical mechanics calculations one takes for the gas Hamiltonian just the Hamiltonian of the free particles, thus neglecting collisions. The role of collisions is subtle: they are the reason for the relaxation to equilibrium but they can be neglected in the final equilibrium averages.

Let us characterize collisions. It is sufficient to consider only binary collisions - collisions between larger collections of particles are negligible because the gas is dilute. The so-called mean free path l_{mean} gives a typical distance that a molecule passes between two collisions. This distance is found by noting that if the particle passes a distance l then on the way it bumps all particles within the cylinder of height l and cross-section d^2. Thus the distance passed to bump into one particle on average is determined from the condition $nl_{mean}d^2 \sim 1$ or

$$l_{mean} \sim \frac{1}{nd^2}. \tag{309}$$

Note that l_{mean} is much larger not only than the molecular size d but also than the mean distance $n^{-1/3}$ between the particles, $l_{mean}n^{1/3} = \epsilon^{-2/3} \gg 1$. The characteristic time that passes between the collisions - the mean free time τ_{mean} is given by $\tau_{mean} \sim l_{mean}/v$ where v is the typical molecular velocity (normally thermal velocity). Collisions occur in spatial regions of typical size $d \ll l_{mean}$ with collision duration time $\tau_{col} \sim d/v \ll \tau_{mean}$. Within the frame of the Boltzmann equation coarse graining is performed over temporal scales much larger than τ_{col} and over spatial scales much larger than d. As a result the collisions are effectively instantaneous in time and local in space. The resulting effective dynamics is qualitatively similar to the dynamics within the model of hard spheres with radius $d/2$. In the latter dynamics the particles are free as long as the distance between their centers exceeds d. At the moment the distance equals d the normal component of the relative velocity of the particles is reversed instantaneously. The arising so-called event-driven dynamics is simple to imagine. One assumes that all coordinates and momenta of the particles are given at some initial time t_0. Propagating these coordinates and momenta in time according to the laws of the free motion one finds the time t_1 of the first collision event, where the distance between a particular pair of particles becomes equal to d. Then updating the velocities of the colliding particles according to the normal component reversal law one repeats the procedure starting with time t_1. Thus the dynamics consists of free motion interrupted by discontinuous changes in particles velocities that take place at discrete moments of time. Within the frame of the Boltzmann equation this applies effectively to all gases.

The Boltzmann equation provides a more fundamental description of the gas dynamics than the hydrodynamics that we considered before. As we will see the latter applies at spatial scales larger than l_{mean} and temporal scales larger than τ_{mean}, while the Boltzmann equation is able in principle to describe motions at smaller scales as well. However, even if the motion occurs at scales describable by the hydrodynamics, its more fundamental description by the Boltzmann equation allows to express the kinetic coefficients of viscosity and heat conductivity (that appear in hydrodynamics as phenomenological constants) in terms of microscopic quantities. Such expressions allow to address the actual calculations of the coefficients.

Like hydrodynamics, the Boltzmann equation applies to gas dynamics in each realization rather than applying just on average to an ensemble of identical systems. The equation applies to the so-called single-particle distribution function $f(\boldsymbol{x}, \boldsymbol{p}, t)$ which definition is rather similar to the definition of the hydrodynamic fields. We first consider a gas without internal degrees of freedom (monoatomic gas). We define a microscopic density

$$f_{micro}(\boldsymbol{x}, \boldsymbol{p}, t) = \sum_{i=1}^{N} \delta(\boldsymbol{x}_i(t) - \boldsymbol{x})\delta(\boldsymbol{p}_i(t) - \boldsymbol{p}), \tag{310}$$

that gives the density of particles with momentum $\boldsymbol{p}$ at point $\boldsymbol{x}$. We have $\int f_{micro}(\boldsymbol{x}, \boldsymbol{p}, t)d\boldsymbol{x}d\boldsymbol{p} = N$. The evolution

of the above density is determined by the equations of motion which are governed by the Hamiltonian

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{j<i} U(|\boldsymbol{r}_i - \boldsymbol{r}_j|). \tag{311}$$

The assumption that the potential is given by the sum of pair interactions is of no limitation because only binary collisions need to be accounted in the considered approximation. The density f_{micro} evolves according to

$$\frac{\partial f_{micro}}{\partial t} + \boldsymbol{v}\frac{\partial f_{micro}}{\partial \boldsymbol{x}} = \left(\frac{\partial f_{micro}}{\partial t}\right)_{col}, \quad \boldsymbol{v} = \frac{\boldsymbol{p}}{m}, \tag{312}$$

where the RHS is due to collisions and it is given by

$$\left(\frac{\partial f_{micro}}{\partial t}\right)_{col} = \frac{\partial}{\partial \boldsymbol{p}} \sum_{i\neq j} \delta(\boldsymbol{x}_i(t) - \boldsymbol{x})\delta(\boldsymbol{p}_i(t) - \boldsymbol{p})\frac{\partial U(|\boldsymbol{x} - \boldsymbol{x}_j(t)|)}{\partial \boldsymbol{x}}. \tag{313}$$

We now define the coarse-grained object, the single-particle distribution function f by

$$f(\boldsymbol{x}, \boldsymbol{p}, t) \equiv \int_{t}^{t+\Delta t} \frac{dt}{\Delta t} \int_{|x'-x|\leq l} \frac{d\boldsymbol{x}'}{V_l} \int_{|p'-p|\leq \Delta p} \frac{d\boldsymbol{p}'}{V_{\Delta p}} f_{micro}(\boldsymbol{x}', \boldsymbol{p}', t'). \tag{314}$$

where V_l, $V_{\Delta p}$ are the volumes of the regions of coarse graining. While $f_{micro}(\boldsymbol{x}, \boldsymbol{p}, t)$ is a function with rather wild dynamics in time, its coarse-grained version obtained with a proper choice of Δt, l and Δp, satisfies a smooth dynamics in much the same way as the hydrodynamic fields do. The function $f(\boldsymbol{x}, \boldsymbol{p}, t)$ counts the partial time-average number of particles $N(\boldsymbol{x}, \boldsymbol{p}, t)$ in a region of the single-particle phase space,

$$N(\boldsymbol{x}, \boldsymbol{p}, t) = f(\boldsymbol{x}, \boldsymbol{p}, t)V_l V_{\Delta p}. \tag{315}$$

This region is a ball with radius l near $\boldsymbol{x}$ and a ball with radius Δp near $\boldsymbol{p}$. The choice of Δp is done so that the variation of $f(\boldsymbol{x}, \boldsymbol{p}, t)$ over the scale Δp in momentum space is negligible and one has

$$\int_{t}^{t+\Delta t} \frac{dt}{\Delta t} \int_{|x'-x|\leq l} \frac{d\boldsymbol{x}'}{V_l} \int_{|p'-p|\leq \Delta p} \frac{d\boldsymbol{p}'}{V_{\Delta p}} \boldsymbol{v}'\nabla' f_{micro}(\boldsymbol{x}', \boldsymbol{p}', t') \approx \boldsymbol{v}\nabla f(\boldsymbol{x}, \boldsymbol{p}, t). \tag{316}$$

Still Δp should not be too small: the consistent definition of f is only possible in the quasi-classical approximation and Δp must be much larger than the scale of momentum quantization $\hbar/l$. The time-derivative of $f(\boldsymbol{x}, \boldsymbol{p}, t)$, similarly to the one of $f_{micro}(\boldsymbol{x}, \boldsymbol{p}, t)$ see Eq. (312), is given by

$$\frac{\partial f}{\partial t} = -\boldsymbol{v}\frac{\partial f}{\partial \boldsymbol{x}} + \left(\frac{\partial f}{\partial t}\right)_{col}, \tag{317}$$

where the first term on the RHS describes the change in $N(\boldsymbol{x}, \boldsymbol{p}, t)$ caused by the ballistic streaming of the particles out of V_l. The understand the second term, due to the collisions, we consider the choice of Δt and l. The choice of l is done according to $l \gg n^{-1/3}$ so that V_l contains a large number of particles. This makes f change only due to averaged effect of many collisions, see below. The choice of Δt is done so that $\tau_{col} \ll \Delta t \ll \tau_{mean}$. Then due to $\tau_{col} \ll \Delta t$ the collisions occur effectively instantaneously while due to $\Delta t \ll \tau_{mean}$ the fraction of particles undergoing collisions in Δt is small. Then the change of f due to collisions can be described differentially and the fraction $(\Delta N(\boldsymbol{x}, \boldsymbol{p}, t)/\Delta t)_{col}$ in

$$\left(\frac{\partial f}{\partial t}\right)_{col} \approx \frac{1}{V_l V_{\Delta p}} \left(\frac{\Delta N(\boldsymbol{x}, \boldsymbol{p}, t)}{\Delta t}\right)_{col}, \tag{318}$$

is well-defined. Here ΔN describes the variation due to collisions of the number of particles in $V_l V_{\Delta p}$ within time Δt. This variation is composed of two parts. First part is due to collisions that particles with momentum $\boldsymbol{p}$ undergo with other particles: such collisions produce particles with momenta generally different from $\boldsymbol{p}$ and decrease $N(\boldsymbol{x}, \boldsymbol{p}, t)$. To describe the corresponding change of N we introduce the number of collisions dN_c that occur per unit time, within the "physically infinitesimal" volume dV (that is dV that contains many particles but such that $f(\boldsymbol{x}, \boldsymbol{p}, t)$ changes negligibly over it) such that particles momenta $\boldsymbol{p}$, $\boldsymbol{p}_1$ are changed to $\boldsymbol{p}'$, $\boldsymbol{p}'_1$

$$dN_c = w(\boldsymbol{p}', \boldsymbol{p}'_1; \boldsymbol{p}, \boldsymbol{p}_1)f f_1 d\boldsymbol{p} d\boldsymbol{p}_1 d\boldsymbol{p}' d\boldsymbol{p}'_1 dV, \tag{319}$$

where $d\boldsymbol{p}$, $d\boldsymbol{p}_1$, $d\boldsymbol{p}'$, $d\boldsymbol{p}_1'$ describe indeterminacy in the particles momenta, $f = f(\boldsymbol{x}, \boldsymbol{p}, t)$ and $f_1 = f(\boldsymbol{x}, \boldsymbol{p}, t)$ (similar notations for f will be used below). The number of collisions is naturally proportional to the number of pairs of particles ff_1 with initial momenta $\boldsymbol{p}$, $\boldsymbol{p}_1$ and to the volume factors. The factor $w(\boldsymbol{p}', \boldsymbol{p}_1'; \boldsymbol{p}, \boldsymbol{p}_1)$ comes from mechanics: it describes the scattering of two particles and can be found by solving the (quantum) mechanical scattering problem. Note that initial momenta are written to the right as it is customary in quantum mechanics. To illustrate Eq. (319) let us consider its use for the derivation of the detailed balance property of the equilibrium state of the gas.

A. Detailed balance

The principle of the detailed balance says that the time-reversal invariance of the equilibrium state in fact holds on the level of elementary processes: on average the changes in the system caused by each elementary process are balanced by the change due to the time-reversed process. For gas this signifies that in equilibrium the average number of transitions from $\boldsymbol{p}$, $\boldsymbol{p}_1$ to $\boldsymbol{p}'$, $\boldsymbol{p}_1'$ is equal to the average number of transitions from $-\boldsymbol{p}'$, $-\boldsymbol{p}_1'$ to $-\boldsymbol{p}$, $-\boldsymbol{p}_1$ (minus comes from time-reversal of momenta). Designating the equilibrium distribution function f by $f_0(\boldsymbol{x}, \boldsymbol{p})$ we find the condition of detailed balance

$$w(\boldsymbol{p}', \boldsymbol{p}_1'; \boldsymbol{p}, \boldsymbol{p}_1) f_0 f_{01} d\boldsymbol{p} d\boldsymbol{p}_1 d\boldsymbol{p}' d\boldsymbol{p}_1' dV = w(-\boldsymbol{p}, -\boldsymbol{p}_1; -\boldsymbol{p}', -\boldsymbol{p}_1') f_0' f_{01}' d\boldsymbol{p} d\boldsymbol{p}_1 d\boldsymbol{p}' d\boldsymbol{p}_1' dV, \tag{320}$$

or

$$w(\boldsymbol{p}', \boldsymbol{p}_1'; \boldsymbol{p}, \boldsymbol{p}_1) f_0 f_{01} = w(-\boldsymbol{p}, -\boldsymbol{p}_1; -\boldsymbol{p}', -\boldsymbol{p}_1') f_0' f_{01}'. \tag{321}$$

Note that due to mechanical reversibility we have

$$w(\boldsymbol{p}', \boldsymbol{p}_1'; \boldsymbol{p}, \boldsymbol{p}_1) = w(-\boldsymbol{p}, -\boldsymbol{p}_1; -\boldsymbol{p}', -\boldsymbol{p}_1'). \tag{322}$$

Let us verify the the Boltzmann distribution

$$f_0(\boldsymbol{x}, \boldsymbol{p}) = const \exp\left[-\frac{p^2}{2mk_BT}\right], \tag{323}$$

indeed validates Eq. (321). We note that $w(\boldsymbol{p}', \boldsymbol{p}_1'; \boldsymbol{p}, \boldsymbol{p}_1)$ should vanish for values of $\boldsymbol{p}$-s that violate conservation of total momentum and energy that is

$$w(\boldsymbol{p}', \boldsymbol{p}_1'; \boldsymbol{p}, \boldsymbol{p}_1) \propto \delta\left(\frac{p^2}{2m} + \frac{p_1^2}{2m} - \frac{p'^2}{2m} - \frac{(p_1')^2}{2m}\right) \delta\left(\boldsymbol{p} + \boldsymbol{p}_1 - \boldsymbol{p}' - \boldsymbol{p}_1'\right). \tag{324}$$

Then equality in Eq. (321) holds due to the first $\delta-$function above. In fact the presence of the second $\delta-$function allows for the more general solution to the detailed balance condition

$$f_0(\boldsymbol{x}, \boldsymbol{p}) = const \exp\left[-\frac{p^2/2m - \boldsymbol{p} \cdot \boldsymbol{V}}{2mk_BT}\right], \tag{325}$$

where $\boldsymbol{V}$ is an arbitrary constant vector. The above solution can be rewritten as

$$f_0(\boldsymbol{x}, \boldsymbol{p}) = const' \exp\left[-\frac{m(\boldsymbol{v} - \boldsymbol{V})^2}{2k_BT}\right], \tag{326}$$

and it corresponds to the Maxwell distribution as seen in the frame moving at speed $\boldsymbol{V}$. Let us note that the detailed balance demand refers only to an average number of processes and not exact the exact one. How does this enter the above consideration? The point is that (323) is true only on average - in reality there are always fluctuations of $f(\boldsymbol{x}, \boldsymbol{p}, t)$ even in equilibrium. Such fluctuations are neglected here from the very beginning and they are also neglected in the frame of the Boltzmann equation.

B. The Boltzmann equation

We are now ready to describe $(\Delta N(\boldsymbol{x}, \boldsymbol{p}, t)/\Delta t)_{col}$ in Eq. (318). It is given by

$$\left(\frac{\Delta N(\boldsymbol{x}, \boldsymbol{p}, t)}{\Delta t}\right)_{col} = -V_l V_{\Delta p} \int w(\boldsymbol{p}', \boldsymbol{p}_1'; \boldsymbol{p}, \boldsymbol{p}_1) ff_1 d\boldsymbol{p}_1 d\boldsymbol{p}' d\boldsymbol{p}_1' + V_l V_{\Delta p} \int w(\boldsymbol{p}, \boldsymbol{p}_1; \boldsymbol{p}', \boldsymbol{p}_1') f' f_1' d\boldsymbol{p}_1 d\boldsymbol{p}' d\boldsymbol{p}_1'. \tag{327}$$

The first term in the RHS describes the decrease of N due to collisions of particles with momentum $\boldsymbol{p}$ with particles with momentum $\boldsymbol{p}_1$ and its meaning was explained above. The second term describes the increase of $N(\boldsymbol{x}, \boldsymbol{p}, t)$ due to collisions of two particles with momenta $\boldsymbol{p}'$ and $\boldsymbol{p}'_1$ that result in one of the particles carrying momentum $\boldsymbol{p}$. Comparing the above with Eq. (318) we find the Boltzmann equation that describes the evolution of $f(\boldsymbol{x}, \boldsymbol{p}, t)$ according to

$$\frac{\partial f}{\partial t} + \boldsymbol{v}\frac{\partial f}{\partial \boldsymbol{x}} = Stf, \tag{328}$$

where the so-called collision integral Stf describes the effect of collisions and it can be written as

$$Stf = \int (w'f'f'_1 - wff_1)d\boldsymbol{p}d\boldsymbol{p}'d\boldsymbol{p}'_1, \quad w = w(\boldsymbol{p}', \boldsymbol{p}'_1; \boldsymbol{p}, \boldsymbol{p}_1), \quad w' = w(\boldsymbol{p}, \boldsymbol{p}_1; \boldsymbol{p}', \boldsymbol{p}'_1). \tag{329}$$

One can rewrite the above integral in a different form using unitarity. This is done more conveniently using quantum mechanical notations. We use the scattering matrix S that describes the probability amplitudes of different scattering processes. This matrix is unitary so that $S^+S = 1$ and we have

$$\sum_n S^*_{ni}S_{nk} = \delta_{ik}, \quad \sum_n |S_{ni}|^2 = 1, \tag{330}$$

where the latter equality follows from the former by setting $i = k$. Since $|S_{ni}|^2$ describes the probability of the transition from i to n then $\sum_n |S_{ni}|^2 = 1$ just expresses that the sum of the probabilities of passing somewhere is one. On the other hand writing the unitarity condition in the form $SS^+ = 1$ we find $\sum_n S_{in}S^*_{kn} = \delta_{ik}$ and

$$\sum_n |S_{in}|^2 = 1, \tag{331}$$

that is the sum of probabilities of transitions to a given final state is also one. It follows that $\sum_n |S_{in}|^2 = \sum_n |S_{ni}|^2$. Excluding in the sum the $i = n$ term which is the same on both sides we obtain

$$\sum_{n \neq i} |S_{in}|^2 = \sum_{n \neq i} |S_{ni}|^2. \tag{332}$$

This condition written in terms of w takes the form

$$\int w(\boldsymbol{p}', \boldsymbol{p}'_1; \boldsymbol{p}, \boldsymbol{p}_1)d\boldsymbol{p}'d\boldsymbol{p}'_1 = \int w(\boldsymbol{p}, \boldsymbol{p}_1; \boldsymbol{p}', \boldsymbol{p}'_1)d\boldsymbol{p}'d\boldsymbol{p}'_1. \tag{333}$$

Noting that the integral over $\boldsymbol{p}'$, $\boldsymbol{p}'_1$ in the second term in Stf in Eq. (329) does not involve f and using the identity above we may rewrite the collision integral as

$$Stf = \int w' \left[f'f'_1 - ff_1 \right] d\boldsymbol{p}_1 d\boldsymbol{p}'d\boldsymbol{p}'_1. \tag{334}$$

The above form is particularly convenient to see that the collision integral vanishes for the shifted Maxwell distribution described by Eq. (326) (and thus of course also the non-sifted distribution). This is seen from the proportionality of w' to δ-functions in energy and momenta like in the analysis of the detailed balance condition. Thus we see immediately from the above form that the equilibrium solutions described by Eq. (326) are stationary solutions of the Boltzmann equation.

It is possible to incorporate external fields in the Boltzmann description easily. For example if an external potential U is applied to the gas and U changes slowly over the scale l then the modified Boltzmann equation is

$$\frac{\partial f}{\partial t} + \boldsymbol{v}\frac{\partial f}{\partial \boldsymbol{x}} - \frac{\partial U}{\partial \boldsymbol{x}}\frac{\partial f}{\partial \boldsymbol{p}} = Stf, \tag{335}$$

where the last term on the LHS accounts for the changes in $N(\boldsymbol{x}, \boldsymbol{p}, t)$ due to the external force driving of $\boldsymbol{p}$. In particular, external potential is a way to include rigid walls into the consideration. Below we don't write down the external forces term which can be included simply.

Why does $f(\boldsymbol{x}, \boldsymbol{p}, t)$ obeys a closed dynamics? As we mentioned velocity of a single particle is almost integral of motion: it is conserved most of the time. Still velocity by itself is not a slow variable because it undergoes fast changes in collisions. To turn it into a slow variable one introduces the collective variable $f(\boldsymbol{x}, \boldsymbol{p}, t)$ which is similar to particle velocity averaged over many particles. Such function is already undergoing only slow changes (over the scale

τ_{mean}) and it represents a slow variable obeying a closed dynamics. The derivation of the closed dynamics involves an essential assumption which we discuss after the derivation of a main consequence of Eq. (328) - the famous H-theorem by Boltzmann. To describe the theorem in its general form we first generalize the description to gases with internal degrees of freedom. A simplest example is a diatomic gas where besides the translational center of mass degree of freedom one needs to account for the rotational degree of freedom of the molecule. In this case collisions generally change not only $\boldsymbol{p}$ but also the angular momentum of the molecule $\boldsymbol{M}$. In contrast, $\boldsymbol{M}$ is conserved between the collisions. It turns out that in this case it is sufficient to include $\boldsymbol{M}$ in the independent arguments of f while the angle coordinates are not essential. Generally, for molecular gases with internal degrees of freedom the Boltzmann equation applies to $f(\boldsymbol{x}, \Gamma, t)$ where Γ includes all integrals of the free motion of the molecule (for diatomic gas $\Gamma = (\boldsymbol{p}, \boldsymbol{M})$). The equation still has the form of Eq. (328) with the collision integral given by

$$St f = \int (w' f' f_1' - w f f_1) d\Gamma d\Gamma' d\Gamma_1', \quad w = w(\Gamma', \Gamma_1'; \Gamma, \Gamma_1), \quad w' = w(\Gamma, \Gamma_1; \Gamma', \Gamma_1'), \tag{336}$$

where w now characterizes the transitions in Γ. As for monoatomic gases, using unitarity one finds an equivalent form of $St f$ given by

$$St f = \int w' \left[f' f_1' - f f_1 \right] d\Gamma_1 d\Gamma' d\Gamma_1'. \tag{337}$$

Again one can see that $St f$ vanishes for the equilibrium distribution.

IX. THE H-THEOREM

The celebrated $H-$theorem by Boltzmann describes a main implication of Eq. (328): within the frame of the Boltzmann equation the information is no longer conserved and entropy grows. In other words, there is finite memory within the frame of the equation. Thus in contrast to the microscopic dynamics which is completely time-reversible, the dynamics described by the Boltzmann equation is irreversible and leads to forgetting of the initial conditions. This is in accord with the general expectation that a passage to a reduced description involves loss of information and the missing information (equivalent to entropy) will grow in the course of evolution. Here the reduced description of the gas dynamics is performed in terms of the single-particle distribution function $f(\boldsymbol{r}, \boldsymbol{\Gamma})$ in contrast to its complete description in terms of the coordinates and the momenta of the particles. We will discuss the origin of irreversibility more below.

Boltzmann considered an "H-function" which is minus the entropy S of the gas. The entropy in terms of the single-particle distribution function $f(\boldsymbol{r}, \Gamma, t)$ is given by

$$S = \int f \ln \left(\frac{e}{f} \right) dV d\Gamma. \tag{338}$$

Clearly S is a function of the state of the gas and the gas evolution is associated with some variation of S in time. This variation obeys

$$\frac{dS}{dt} = -\int \ln f \frac{\partial f}{\partial t} dV d\Gamma = \int \ln f \boldsymbol{v} \frac{\partial f}{\partial \boldsymbol{x}} dV d\Gamma + \left(\frac{dS}{dt} \right)_{col}, \tag{339}$$

where the last term describes the change of S due to collisions,

$$\left(\frac{dS}{dt} \right)_{col} = -\int \ln f \left(\frac{\partial f}{\partial t} \right)_{col} dV d\Gamma = -\int \ln f St f dV d\Gamma. \tag{340}$$

For the first term in the RHS of Eq. (339) one has

$$\int \ln f \boldsymbol{v} \frac{\partial f}{\partial \boldsymbol{x}} dV d\Gamma = \int \boldsymbol{v} \frac{\partial}{\partial \boldsymbol{x}} f \ln \frac{f}{e} dV d\Gamma = 0, \tag{341}$$

where we assumed that the integral of the total derivative vanishes. We conclude that entropy changes only due to collisions,

$$\frac{dS}{dt} = \left(\frac{dS}{dt} \right)_{col} = \int \dot{s} d\boldsymbol{x}, \tag{342}$$

where we defined the density $\dot{s}$ of entropy production due to collisions by

$$\dot{s}(\boldsymbol{x}, t) = -\int \ln f \, St f \, d\Gamma. \tag{343}$$

To study the above expression we consider properties of the collision integral.

A. Some properties of the collision integral

Let us derive a useful transformation for integrals of the form $\int \phi(\Gamma) St f \, d\Gamma$ where ϕ is an arbitrary function. Using the collision integral in the form (336) we have

$$\int \phi(\Gamma) St f \, d\Gamma = \int \phi(\Gamma) w(\Gamma, \Gamma_1; \Gamma', \Gamma_1') f' f_1' \, d^4\Gamma - \int \phi(\Gamma) w(\Gamma', \Gamma_1'; \Gamma, \Gamma_1) f f_1 \, d^4\Gamma. \tag{344}$$

where $d^4\Gamma \equiv d\Gamma \, d\Gamma_1 \, d\Gamma' \, d\Gamma_1'$. Interchanging in the second integral Γ and Γ_1 with Γ' and Γ_1' we find

$$\int \phi(\Gamma) St f \, d\Gamma = \int \left[\phi(\Gamma) - \phi(\Gamma') \right] w(\Gamma, \Gamma_1; \Gamma', \Gamma_1') f' f_1' \, d^4\Gamma. \tag{345}$$

Next we interchange Γ with Γ_1 and Γ' with Γ_1' in the last integral and obtain

$$\int \left[\phi(\Gamma) - \phi(\Gamma') \right] w(\Gamma, \Gamma_1; \Gamma', \Gamma_1') f' f_1' \, d^4\Gamma = \int \left[\phi(\Gamma_1) - \phi(\Gamma_1') \right] w(\Gamma, \Gamma_1; \Gamma', \Gamma_1') f' f_1' \, d^4\Gamma, \tag{346}$$

where we use that $w(\Gamma, \Gamma_1; \Gamma', \Gamma_1') = w(\Gamma_1, \Gamma; \Gamma_1', \Gamma')$. The latter equality follows from the fact that w on both sides of the equation describe the same scattering event with the only change of which particle to refer to as the "first" and which as the "second". Taking half sum of Eq. (346) we obtain the final result

$$\int \phi(\Gamma) St f \, d\Gamma = \frac{1}{2} \int \left[\phi(\Gamma) + \phi(\Gamma_1) - \phi(\Gamma') - \phi(\Gamma_1') \right] w(\Gamma, \Gamma_1; \Gamma', \Gamma_1') f' f_1' \, d^4\Gamma. \tag{347}$$

By taking $\phi = 1$ we find from the above equation that

$$\int St f \, d\Gamma = 0. \tag{348}$$

Two additional integrals vanish as well,

$$\int \epsilon(\Gamma) St f \, d\Gamma = 0, \quad \int \boldsymbol{p} \, St f \, d\Gamma = 0, \tag{349}$$

which is seen by noting that w in Eq. (347) is non-vanishing only for those values of Γ which obey the energy conservation $\epsilon(\Gamma) + \epsilon(\Gamma_1) = \epsilon(\Gamma') + \epsilon(\Gamma_1')$ and the momentum conservation $\boldsymbol{p} + \boldsymbol{p}_1 = \boldsymbol{p}' + \boldsymbol{p}_1'$. Let us show the meaning of equations (348)-(349). We introduce the particle concentration $N(\boldsymbol{x}, t)$, the energy density $N(\boldsymbol{x}, t)\epsilon(\boldsymbol{x}, t)$ and the momentum density $\rho(\boldsymbol{x}, t)\boldsymbol{V}(\boldsymbol{x}, t)$ where $\rho(\boldsymbol{x}, t) = mN(\boldsymbol{x}, t)$ is the mass density. These can be expressed with the help of the single-particle distribution function $f(\boldsymbol{r}, \Gamma, t)$ as

$$N(\boldsymbol{x}, t) = \int f(\boldsymbol{x}, \Gamma, t) d\Gamma, \quad N(\boldsymbol{x}, t)\epsilon(\boldsymbol{x}, t) = \int \epsilon(\Gamma) f(\boldsymbol{x}, \Gamma, t) d\Gamma, \quad \rho(\boldsymbol{x}, t)\boldsymbol{V}(\boldsymbol{x}, t) = \int \boldsymbol{p} f(\boldsymbol{x}, \Gamma, t) d\Gamma. \tag{350}$$

Then Eqs. (348)-(349) tell that the rates of change of the above densities due to the collisions vanish,

$$\left(\frac{\partial N}{\partial t} \right)_{col} = \int \left(\frac{\partial f}{\partial t} \right)_{col} d\Gamma = \int St f \, d\Gamma = 0, \quad \left(\frac{\partial (N\epsilon)}{\partial t} \right)_{col} = \int \epsilon(\Gamma) \left(\frac{\partial f}{\partial t} \right)_{col} d\Gamma = \int \epsilon(\Gamma) St f \, d\Gamma = 0, \tag{351}$$

$$\left(\frac{\partial (\rho \boldsymbol{V})}{\partial t} \right)_{col} = \int \boldsymbol{p} \left(\frac{\partial f}{\partial t} \right)_{col} d\Gamma = \int \boldsymbol{p} \, St f \, d\Gamma = 0. \tag{352}$$

In other words, collisions happening within a physically infinitesimal volume dV do not change the total number of particles, energy and momentum inside the volume. An additional property of the collision integral follows from Eq. (347), namely that

$$\int \ln f \, St f \, d\Gamma = -\frac{1}{2} \int w' f' f_1' \ln \left(\frac{f' f_1'}{f f_1} \right) d^4\Gamma \leq 0. \tag{353}$$

To see the inequality we note that Eq. (348) applied to collision integral in the form (337) produces the identity

$$\int w'(f'f_1' - ff_1)d^4\Gamma = \int w'ff_1\left[x - 1\right] = 0, \quad x \equiv \frac{f'f_1'}{ff_1}. \tag{354}$$

Using the above identity we may rewrite Eq. (353) and obtain

$$\int \ln f St f d\Gamma = -\frac{1}{2}\int w'ff_1\left[x\ln x - x + 1\right]d^4\Gamma \le 0, \tag{355}$$

where the equality holds if and only if $x = 1$, see Eq. (297). It is the last property of the collision integral that underlies the $H-$theorem.

B. Proof of $H-$theorem

We are now ready to complete the proof of the $H-$theorem. We find from Eq. (342) that

$$\frac{dS}{dt} = \int \dot{s}d\boldsymbol{x}, \quad \dot{s} = -\int \ln f St f d\Gamma \ge 0, \tag{356}$$

see Eq. (355). Thus the entropy grows always unless $x = 1$ or $ff_1 = f'f_1'$ where the latter equality is satisfied in equilibrium. Let us stress however that the above equation does not imply that in relaxation to equilibrium the gas entropy grows locally everywhere. In fact this is impossible - we could start with an initial state which local entropy density exceeds the equilibrium one in some places. To clarify this point we introduce the entropy density $\tilde{s}$ by

$$S(t) = \int \tilde{s}(\boldsymbol{x}, t)dV, \quad \tilde{s}(\boldsymbol{x}, t) \equiv \int f\ln\left(\frac{e}{f}\right)d\Gamma. \tag{357}$$

We have

$$\frac{\partial \tilde{s}}{\partial t} = \int \ln f \boldsymbol{v}\frac{\partial f}{\partial \boldsymbol{x}}d\Gamma - \int \ln f St f d\Gamma. \tag{358}$$

While the last term is always nonnegative the first one can have an arbitrary sign. In fact in some regions of space it is negative because its spatial integral balances to zero. Thus locally entropy can decrease due to entropy exchange with the nearby regions of the gas which is described by the velocity term above.

We see that the Boltzmann equation is in apparent contradiction with mechanics. Within mechanics there is no function of state which would grow monotonously with time - the existence of such a function would contradict microscopic reversibility. In particular, for gas obeying the Boltzmann equation the Poincare recurrence theorem does not hold. The theorem says that for gas in a finite vessel the system evolution always brings it back arbitrarily close to initial state. The return time is called the Poincare recurrence time. In particular, if initially gas molecules are localized in one half of the vessel then they will return close to this state later. The point where the transition to irreversible equations occurs is Eq. (319). The equation assumes that the number of pairs of particles with given momenta in given volume is given by the product of the single-particle distribution functions. In reality, to describe the number of pairs we need to introduce the two-particle distribution function that gives us directly the number of pairs in the volume. The decomposition into product like in the usual probability theory corresponds to the assumption that the particles are not correlated before the collision. On the other hand, the particles are correlated after the collision. In this way, the Boltzmann equation breaks the symmetry between the moments of time before and after the collision which eventually results in irreversible dynamics. The assumption that molecules have no prior knowledge of each other and are independent before the collision is known as the molecular chaos assumption. Note the resemblance to the quantum mechanical rule of measurement which was observed by one of the students.

What does the Boltzmann equation describe in view of the above? In reality sooner or later the molecules which collided in the past and are thus correlated will collide again. The time when it happens is on average expected to be comparable with Poincare recurrence time. There is an additional effect that the correlation between the molecules spreads in the gas due to collisions with molecules that will collide with both of the particles. In this way the memory of the initial state stays in the gas. The time-scale at which the effects of this memory are expected to be visible is the Poincare recurrence time which is huge for large number of molecules. At ordinary time-scales the assumption that colliding molecules are not correlated works well. Thus the Boltzmann equation describes what happens at ordinary time-scales most of the time (i. e. assuming that we are not close to the time when memory effects start playing role). This is in accord with the basic understanding of the laws of thermodynamics as not absolute.

X. HYDRODYNAMICS AS UNIVERSAL DESCRIPTION OF SOLUTIONS TO THE BOLTZMANN EQUATION AT LARGE TIMES

The fact that collisions increase the entropy locally allows to reach much insight into the gas evolution. Below we perform the consideration for gas with no internal degrees of freedom.

The local relaxation to equilibrium due to collisions is constrained by the laws of conservation of mass, energy and momentum expressed by Eqs. (352). To see the consequences of such constrained local relaxation consider first the evolution of the gas from the initial condition on f that corresponds to constant densities of mass, energy and momentum so that $N(\boldsymbol{x}, t = 0)$, $\epsilon(\boldsymbol{x}, t = 0)$ and $\boldsymbol{V}(\boldsymbol{x}, t = 0)$ defined by Eqs. (350) are constants. In this case the gas will relax to equilibrium during the characteristic time-scale of collisions τ_{mean}. This is summarized by the so-called relaxation time approximation where the collision integral is substituted by

$$ St f \approx -\frac{f - f_0}{\tau}, \tag{359} $$

with $\tau \sim \tau_{mean}$ and f_0 the local equilibrium distribution function, see below. In contrast, the relaxation time increases greatly when $N(\boldsymbol{x}, t = 0)$, $\epsilon(\boldsymbol{x}, t = 0)$ and $\boldsymbol{V}(\boldsymbol{x}, t = 0)$ vary in space. Assume first that the scale L of variations of $N(\boldsymbol{x}, t = 0)$, $\epsilon(\boldsymbol{x}, t = 0)$ and $\boldsymbol{V}(\boldsymbol{x}, t = 0)$ is very large. In this case the gas locally does not know that somewhere far away the values of $N(\boldsymbol{x}, t = 0)$, $\epsilon(\boldsymbol{x}, t = 0)$ and $\boldsymbol{V}(\boldsymbol{x}, t = 0)$ are different from the local ones. The gas will relax within characteristic time-scale τ_{mean} to the state which has the form of the local equilibrium with $f(\boldsymbol{x}, \boldsymbol{p})$ obeying

$$ f(\boldsymbol{x}, \boldsymbol{p}) \approx f_0(\boldsymbol{x}, \boldsymbol{p}, t = 0) = \frac{N(\boldsymbol{x}, t = 0)}{[2\pi m k_B T(\boldsymbol{x}, t = 0)]^{3/2}} \exp\left[-\frac{m(\boldsymbol{v} - \boldsymbol{V}[\boldsymbol{x}, t = 0])^2}{2k_B T(\boldsymbol{x}, t = 0)}\right], \tag{360} $$

where $T(\boldsymbol{x}, t = 0)$ is fixed by the demand that the distribution function above reproduces the correct value of the energy density,

$$ \epsilon(\boldsymbol{x}, t = 0) = \frac{1}{N(\boldsymbol{x}, t = 0)} \int \frac{m v^2}{2} f(\boldsymbol{x}, \boldsymbol{p}) d\boldsymbol{p} = \frac{m V(\boldsymbol{x}, t = 0)^2}{2} + \frac{3 k_B T(\boldsymbol{x}, t = 0)}{2}, \tag{361} $$

where the first term in the RHS represents the center of mass energy. To see the above formally note that by the assumption of large L the spatial gradient term in the Boltzmann equation (328) is much smaller than the collision integral so that initially the Boltzmann equation gives $\partial_t f \approx St f$. The latter evolution is purely in momentum variable with $f(\boldsymbol{x}, \boldsymbol{p})$ evolving independently at different $\boldsymbol{x}$. This evolution continues until f becomes of the form $f = f_0 + \delta f$ where $St[f_0 + \delta f] \sim v \nabla f_0$ (remember that $St f_0 = 0$ so that $St[f_0 + \delta f] \sim \delta f$). At this point the gradient term becomes important in the Boltzmann equation while f_0 has the form given by Eq. (360) with $N(\boldsymbol{x})$, $\epsilon(\boldsymbol{x})$ and $\boldsymbol{V}(\boldsymbol{x})$ given by their original local values at $t = 0$. Once this happens (within a characteristic time-scale τ_{mean}) further evolution starts to change the local values of the conserved quantities that is $f(\boldsymbol{x}, \boldsymbol{p}, t)$ obeys

$$ f(\boldsymbol{x}, \boldsymbol{p}, t) = f_0(\boldsymbol{x}, \boldsymbol{p}, t) + \delta f, \quad f_0(\boldsymbol{x}, \boldsymbol{p}, t) = \frac{N(\boldsymbol{x}, t)}{[2\pi m k_B T(\boldsymbol{x}, t)]^{3/2}} \exp\left[-\frac{m(\boldsymbol{v} - \boldsymbol{V}[\boldsymbol{x}, t])^2}{2k_B T(\boldsymbol{x}, t)}\right], \quad \delta f \ll f_0, \tag{362} $$

where $N(\boldsymbol{x}, t)$, $\boldsymbol{V}(\boldsymbol{x}, t)$ and $T(\boldsymbol{x}, t)$ depend in time. The evolution of the latter fields is due to the combined action of the ballistic motion, that mixes them among different regions of the gas, and the local relaxation due to collisions, that keeps the approximate local equilibrium form given by Eq. (362) intact. The characteristic scale of this evolution is the mixing time $\tau_{mix} \sim L/v \sim \tau_{mean}(L/l_{mean})$. During this time-scale gas molecules moving at the characteristic speed v will mix the locally conserved quantities which inhomogeneity scale is L. It is now clear how large L should be for the above picture to hold: it should be such that $\tau_{mean} \ll \tau_{mix}$ or $l_{mean}/L \ll 1$. The parameter l_{mean}/L is called the Knudsen number Kn. If the initial conditions are such that $Kn \ll 1$ then after a time-scale of order τ_{mean} the distribution function takes the form described by Eq. (362). In particular, if one is not interested in the details of the initial transient at time-scale τ_{mean} one can use directly Eq. (362) and address the evolution of $N(\boldsymbol{x}, t)$, $\boldsymbol{V}(\boldsymbol{x}, t)$ and $T(\boldsymbol{x}, t)$. This evolution is described by the equations of hydrodynamics and it is discussed in the next subsection. Note that the final result of the hydrodynamic evolution must be that $N(\boldsymbol{x})$, $\boldsymbol{V}(\boldsymbol{x})$ and $T(\boldsymbol{x})$ are constant while δf in Eq. (362) vanishes. The relaxation time is at least $\tau_{mix} \gg \tau_{mean}$ and sometimes much larger.

Thus we saw that if initial conditions for the Boltzmann equation are such that $Kn \ll 1$ then at $t \gg \tau_{mean}$ the distribution function is described by Eq. (362) and the equations of hydrodynamics. Let us show that in fact such description holds at $t \gg \tau_{mean}$ for arbitrary initial conditions, including those with $Kn \gtrsim 1$. The ultimate reason for this can be seen from the theory of hydrodynamic fluctuations that demonstrates the robust property that the higher the wave-number of the perturbation, the faster it relaxes. As a result the evolution of Kn with time brings us to

the region with $Kn \ll 1$ where Eq. (362) starts to apply. The evolution of $N(\boldsymbol{x},t)$, $\boldsymbol{V}(\boldsymbol{x},t)$ and $T(\boldsymbol{x},t)$ proceeds as follows. During time-scale of collisions τ_{mean} the initial fields become smooth over the scale l_{mean} and Kn becomes of order one. During further evolution the combined action of the ballistic motions and collisions gradually eats the higher-wavenumber components of $N(\boldsymbol{x},t)$, $\boldsymbol{V}(\boldsymbol{x},t)$ and $T(\boldsymbol{x},t)$ unless the regime with $Kn \ll 1$ settles down at $t \gg \tau_{mean}$. The difference between the cases where the initial conditions obey $Kn \ll 1$ and $Kn \gtrsim 1$ is that in the latter case one does not know the effective initial conditions for $N(\boldsymbol{x},t)$, $\boldsymbol{V}(\boldsymbol{x},t)$ and $T(\boldsymbol{x},t)$ in Eq. (362) without going into the details of the transient regime. For initial $Kn \ll 1$ these conditions are determined just by the exact values of the locally conserved quantities at $t = 0$.

Thus a reduced description of the gas dynamics is possible at $t \gg \tau_{mean}$ where instead of one scalar function of six variables one can use five scalar functions, $N(\boldsymbol{x},t)$, $\boldsymbol{V}(\boldsymbol{x},t)$ and $T(\boldsymbol{x},t)$ of three variables. This is a big reduction in complexity: instead of $f(\boldsymbol{x},p)$ we use just a few of its low-order momenta in $\boldsymbol{p}$- variable [hydrodynamic fields are moments of f see Eqs.(350)]. We have now three levels of description of gas dynamics, which apply at different temporal and spatial scales. Mechanics (classical or quantum) is the most fundamental level of the description here. The Boltzmann equation is the next level, it provides a description at time-scales larger than the duration of collisions τ_{col} and at spatial scales larger than the range of molecular interactions or the size of the collision regions d. Within the Boltzmann equation collisions are considered as point-like events in space and time. The last, third, level of description is hydrodynamic, it applies at time-scales larger than $\tau_{mean} \gg \tau_{col}$ and at spatial scales much larger than l_{mean}. Let us pass to the derivation of the hydrodynamic evolution equations.

A. The evolution of the hydrodynamic fields

We now address the evolution of densities of locally conserved charges at time-scales much greater than τ_{mean} which is equivalent to the evolution of the hydrodynamic fields $N(\boldsymbol{x},t)$, $\boldsymbol{V}(\boldsymbol{x},t)$ and $T(\boldsymbol{x},t)$. Hydrodynamics will be considered as a certain perturbation series solution of the Boltzmann equation with evolution determined by the demand that the series solves the equation.

First we note by taking the time derivatives of Eqs. (350) with the help of the Boltzmann equation that the following identities hold

$$\frac{\partial \rho(\boldsymbol{x},t)}{\partial t} + \nabla \cdot (\rho \boldsymbol{V}) = 0, \quad \frac{\partial \rho(\boldsymbol{x},t) V_i(\boldsymbol{x},t)}{\partial t} = -\frac{\partial}{\partial x_j} \int m v_i v_j f(\boldsymbol{x},\boldsymbol{p},t) d\boldsymbol{p},$$
$$\frac{\partial N(\boldsymbol{x},t) \epsilon(\boldsymbol{x},t)}{\partial t} = -\frac{\partial}{\partial x_i} \int \frac{m v_i v^2}{2} f(\boldsymbol{x},\boldsymbol{p},t) d\boldsymbol{p}, \tag{363}$$

where we used that the collision integral gives zero contribution into the time derivatives of densities of locally conserved charged, see Eqs. (351)-(352). Above we employed the monoatomic gas expression $\epsilon(\Gamma) = m v^2/2$. The equations above are just consequences of the definition and they apply independently of the dynamics of f. Assumptions on f will allow us to close the equations for the fields $N(\boldsymbol{x},t)$, $\boldsymbol{V}(\boldsymbol{x},t)$ and $T(\boldsymbol{x},t)$. Notice however that the continuity equation determining the evolution of ρ is already closed and needs no further studies. Now if we consider the hydrodynamic regime with f determined by Eq. (362) then it is easy to find that in the leading order

$$\int m v_i v_j f(\boldsymbol{x},\boldsymbol{p},t) d\boldsymbol{p} \approx \int m v_i v_j f_0(\boldsymbol{x},\boldsymbol{p},t) d\boldsymbol{p} = \rho V_i V_j + N k_B T \delta_{ij} = \rho V_i V_j + p \delta_{ij}, \tag{364}$$

where we recognized that $N k_B T$ is the local pressure of the gas. Analogously we have

$$\int \frac{m v_i v^2}{2} f(\boldsymbol{x},\boldsymbol{p},t) d\boldsymbol{p} \approx \int \frac{m v_i v^2}{2} f_0(\boldsymbol{x},\boldsymbol{p},t) d\boldsymbol{p} = \left(\frac{\rho V^2}{2} + \frac{3 N k_B T}{2} \right) V_i + p V_i. \tag{365}$$

Using the expression for ϵ in terms of $N(\boldsymbol{x},t)$, $\boldsymbol{V}(\boldsymbol{x},t)$ and $T(\boldsymbol{x},t)$, see Eq. (361), we find the following equations

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \boldsymbol{V}) = 0, \quad \frac{\partial [\rho V_i]}{\partial t} + \frac{\partial [\rho V_i V_j + p \delta_{ij}]}{\partial x_j} = 0,$$
$$\frac{\partial}{\partial t} \left[\frac{\rho V^2}{2} + \frac{3 N k_B T}{2} \right] + \frac{\partial}{\partial x_i} \left(\left[\frac{\rho V^2}{2} + \frac{3 N k_B T}{2} \right] V_i + p V_i \right) = 0. \tag{366}$$

These are nothing but the ideal hydrodynamics equations of gas with no internal degrees of freedom. Note that the energy flux is given by energy density times V_i, which represents purely convective flux of energy plus the pressure contribution $p V_i$ that represents the work done by the pressure forces. The above equations while describing meaningful

dynamics do not describe relaxation to equilibrium. In particular, the entropy is conserved by the equations of ideal hydrodynamics. In contrast, relaxation dynamics arises in the next order in Kn (which is the small parameter of the hydrodynamic approximation), where $\delta f = f - f_0$ is accounted for in Eqs. (364)-(365).