Non-Equilibrium Continuum Physics **TA session #2**

15/05/2023

Coarse graining (and some leftovers)

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1 Transformation of areal elements

How does $d\boldsymbol{S}$ relate to $d\boldsymbol{s}$? Consider an arbitrary line element $d\boldsymbol{X}$ going through $d\boldsymbol{S}$. The spanned volume is $dV = d\boldsymbol{S} \cdot d\boldsymbol{X}$. Correspondingly, in the deformed coordinates we have $dv = d\boldsymbol{s} \cdot d\boldsymbol{x}$. By definition of the Jacobian, we know that the ratio of the volumes is $dv = J\,dV$. Since $d\boldsymbol{x} = \boldsymbol{F} d\boldsymbol{X}$ we have

$$ds_j F_{ji} dX_i = ds_j dx_j = dv = J dV = J dS_i dX_i \ . \tag{1}$$

Since $d\boldsymbol{X}$ was arbitrary, we get $ds_j F_{ji} = J dS_i$ or in more convenient notation

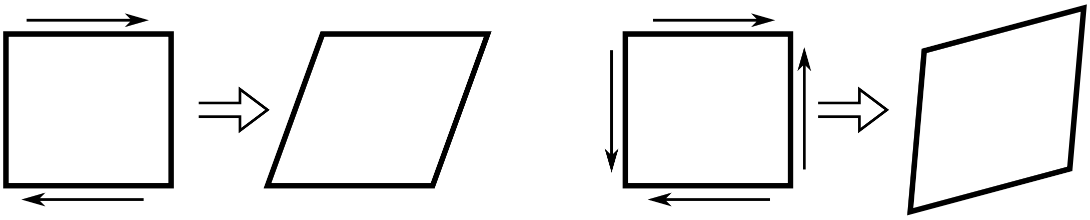
$$\boldsymbol{F}^T d\boldsymbol{s} = J d\boldsymbol{S} \ , \qquad d\boldsymbol{s} = J \boldsymbol{F}^{-T} d\boldsymbol{S} \ . \tag{2}$$

2 Linearized strain under shear

We start by getting some intuition about the geometrical meaning of the linearized strain

$$\varepsilon_{ij} = \frac{1}{2} \left(\partial_i u_j + \partial_j u_i \right) \ , \tag{3}$$

under shear. Two very common strain states are called *pure shear* and *simple shear*. Simple shear is the situation in which displacement in one direction is a linear function of the orthogonal coordinate, as seen in Fig. 1a. Pure shear is the state when the same shear is applied in both direction, as seen in Fig. 1b. In this case there are only shear strains (in some coordinate system), that is, $\boldsymbol{\varepsilon}$ is of the form



(a) Simple shear (b) Pure shear

Figure 1

$$\varepsilon_{ij} = \begin{pmatrix} 0 & \gamma \\ \gamma & 0 \end{pmatrix} \ . \tag{4}$$

What is the relation between simple shear and pure shear? In simple shear, the displacement field is

$$x = X + \gamma Y \ , \qquad\qquad y = Y \ . \tag{5}$$

So the deformation gradient is

$$\boldsymbol{F} = \begin{pmatrix} 1 & \gamma \\ 0 & 1 \end{pmatrix} . \tag{6}$$

This can be decomposed into a state of pure shear and infinitesimal rotation:

$$\boldsymbol{H} = \boldsymbol{F} - \boldsymbol{I} = \underbrace{\begin{pmatrix} 0 & \frac{\gamma}{2} \\ \frac{\gamma}{2} & 0 \end{pmatrix}}_{\text{pure shear}} + \underbrace{\begin{pmatrix} 0 & \frac{\gamma}{2} \\ -\frac{\gamma}{2} & 0 \end{pmatrix}}_{\text{rotation}} . \tag{7}$$

Indeed, it is seen that Fig. 1b is a slightly rotated version of Fig. 1a.

Note that for a deformation that leaves everything in place, i.e. $\boldsymbol{x} = \boldsymbol{X}$, we have $\boldsymbol{F} = \boldsymbol{I}$ and thus $\boldsymbol{H} \equiv \boldsymbol{F} - \boldsymbol{I}$ is what quantifies the non-rigid-body deformation. What we just showed is that $\boldsymbol{F} - \boldsymbol{I}$ can be decomposed to a symmetric part, which is the strain, and an antisymmetric part, which is a rotation and does not cost energy. This is why only the symmetric part of $\boldsymbol{F}$ is used in all versions of strain measures.

Lets focus now on pure shear. We can write the pure shear deformation in one of two forms. We can write

$$\boldsymbol{F}_1 = \begin{pmatrix} 1 & \gamma/2 \\ \gamma/2 & 1 \end{pmatrix} , \tag{8}$$

or as

$$\boldsymbol{F}_2 = \begin{pmatrix} 1+\gamma/2 & 0 \\ 0 & 1-\gamma/2 \end{pmatrix} , \tag{9}$$

both shown in Fig. 2. Let us compare $\boldsymbol{F}_1$ and $\boldsymbol{F}_2$ — their trace $\operatorname{tr}\boldsymbol{F}_1 = 2 = \operatorname{tr}\boldsymbol{F}_2$ and determinant $\det\boldsymbol{F}_1 = 1 - \frac{\gamma^2}{4} = \det\boldsymbol{F}_2$ are exactly the same. This implies that these two deformations are equivalent. By diagoanlizing the two $\boldsymbol{F}$'s we observe their eigenvectors are simply rotated by $\pi/4$ (or, that one can transform one into another with similarity transformation) — they represent the same deformation. It is easy to see that both of these are equivalent to simple shear in the *linear* approximation, but when considering the full *nonlinear* deformation, simple shear *is* volume preserving, while pure shear deformations *are not*.

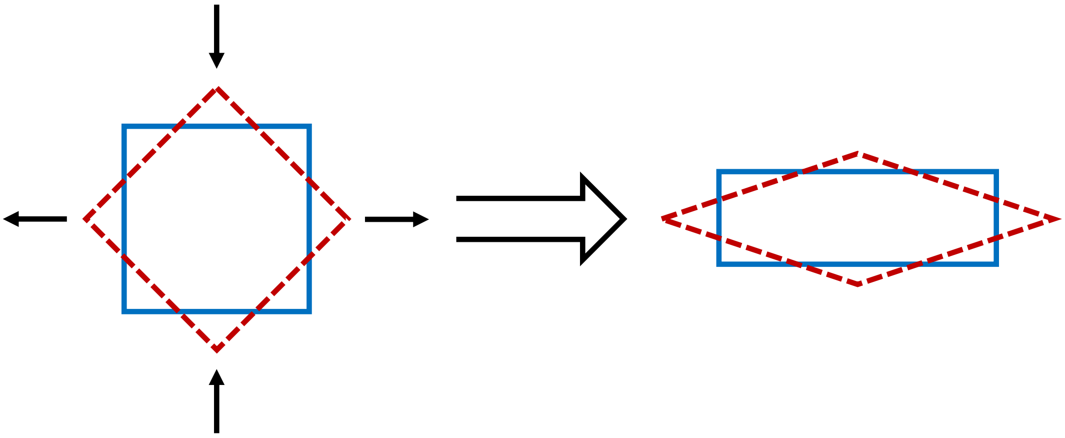


Figure 2

3 Coarse Graining

The main purpose of this section is to see how to develop a continuum theory to describe the deformation of a discrete system, a process known as “coarse graining”. This is also the first time in the course that we’ll develop a *constitutive relation* from microscopic physics, i.e. calculate how the stress depends on the deformation. The system we’ll examine is a two-dimensional triangular lattice of masses and springs, shown in Fig. 3. We assume that the springs are usual linear springs with an identical spring constant k and that in the undeformed state all the springs are at their rest-lengths, which we denote by a.

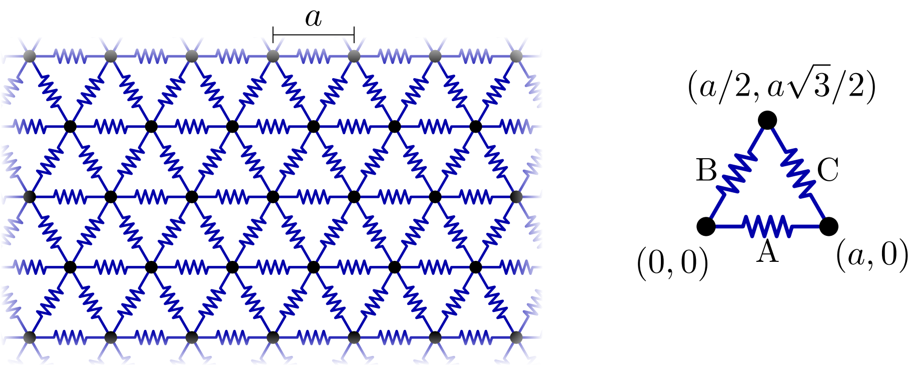


Figure 3: Left: A triangular lattice with a lattice constant a. Right: the unit cell with the coordinates of the vertices.

The central quantity we will want to calculate is the energetic cost of deformation. As you’ve heard from Eran in the last lecture, stresses and strains are intimately related and the observable that relates the two is the energy. Formally, stress and strain are a conjugate variable pair (like many other pairs you know of: pressure-volume, magnetic field-magnetization, chemical potential-particle number etc.).

Assume the material undergoes some motion $\boldsymbol{x} = \boldsymbol{\varphi}(\boldsymbol{X})$. A crucial requirement in coarse graining is that the observables of interest vary slowly in space, much slower than the relevant microscopic degrees of freedom. Formally, this means that the Fourier decomposition of $\boldsymbol{\varphi}$ only has contributions from wavevectors $\boldsymbol{q}$ satisfying $|\boldsymbol{q}a| \ll 1$ (you may have seen a similar requirement when you learned about the Debye model for the phonon contribution to the specific heat). Thus, we assume that we can analyze each small portion of the lattice separately and write the energy density u as a function of the *local values* of the deformation (and its gradients)

$$u(\boldsymbol{r}) = u\Big(\boldsymbol{\varphi}(\boldsymbol{r}), \boldsymbol{F}(\boldsymbol{r}), \nabla\boldsymbol{F}, \ldots\Big) \, . \tag{10}$$

Note that in Eran’s notes energy density is defined per unit mass and here I use densities per unit volume (=area). The two are simply related by a factor ρ. Finally, we can then express the total energy of the system as a volume integral $\mathcal{U} = \int u(\boldsymbol{r}) d^3\boldsymbol{r}$.

So let’s calculate u defined in Eq. (10). Since we do not consider any external fields, the energy must be independent of global translation, i.e. $\boldsymbol{\varphi}$ itself. Also, we consider here only the contribution of $\boldsymbol{F}$ to the energy and neglect higher gradients. This is an "extra" approximation which follows the same spirit of the coarse-graining: if $|\boldsymbol{q}a| \ll 1$ then two adjacent masses will experience roughly the same $\boldsymbol{F}$, and the approximation becomes better when $|\boldsymbol{q}a|$ becomes smaller. Note that it is perfectly "kosher" to consider also terms like $\nabla\boldsymbol{F}$, $\nabla^2\boldsymbol{F}$, etc, but that would require the theory to include explicitly a microscopic lengthscale, something that we would like to avoid at this point.

Examine the unit cell that in the undeformed state is located at $\boldsymbol{X} = 0$. Its vertices are at $\boldsymbol{X}^{(1)} = (0, 0)$, $\boldsymbol{X}^{(2)} = (a, 0)$ and $\boldsymbol{X}^{(3)} = (a/2, a\sqrt{3}/2)$. After the deformation, their positions are

$$\boldsymbol{x}(\boldsymbol{X}) \approx \boldsymbol{F}\boldsymbol{X} + \mathcal{O}(a^2)\ ,\boldsymbol{x}^{(1)} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}, \boldsymbol{x}^{(2)} = a\begin{pmatrix} F_{1,1} \\ F_{2,1} \end{pmatrix}, \boldsymbol{x}^{(3)} = \frac{a}{2}\begin{pmatrix} F_{1,1} + \sqrt{3}F_{1,2} \\ F_{2,1} + \sqrt{3}F_{2,2} \end{pmatrix}\ . \quad (11)$$

The deformed lengths of the three springs denoted by A,B,C in the figure are

$$L_A = \left|\boldsymbol{x}^{(2)} - \boldsymbol{x}^{(1)}\right| = \left|(aF_{1,1}, aF_{2,1})\right| = a\sqrt{{F_{1,1}}^2 + {F_{2,1}}^2}\ , \quad (12)$$

$$L_B = \left|\boldsymbol{x}^{(3)} - \boldsymbol{x}^{(1)}\right| = \frac{a}{2}\sqrt{\left(F_{1,1} + \sqrt{3}F_{1,2}\right)^2 + \left(\sqrt{3}F_{2,2} + F_{2,1}\right)^2}\ , \quad (13)$$

$$L_C = \left|\boldsymbol{x}^{(3)} - \boldsymbol{x}^{(2)}\right| = \frac{a}{2}\sqrt{\left(F_{1,1} - \sqrt{3}F_{1,2}\right)^2 + \left(\sqrt{3}F_{2,2} - F_{2,1}\right)^2}\ . \quad (14)$$

The total energy is given by

$$Su = \frac{1}{2}k\left(L_A - a\right)^2 + \frac{1}{2}k\left(L_B - a\right)^2 + \frac{1}{2}k\left(L_C - a\right)^2\ , \quad (15)$$

where $S = a^2\sqrt{3}/2$ is twice the area of the unit cell[1]. It's easy to see that if $\boldsymbol{F} = \boldsymbol{I}$ then $L_i = a$ and clearly the energy will vanish, as expected.

Let us examine this energy function. The first thing we note about u is that it doesn't look like a "tensor function", i.e. it seems to depend on all the entries of $\boldsymbol{F}$ in some kind of a nasty manner that cannot be written in a nice geometrical form like $f(\operatorname{tr}\boldsymbol{F}, \det\boldsymbol{F}, \boldsymbol{F}:\boldsymbol{F}, \cdots)$. Second, it seems that, unlike what we said in the last TA session, it seems to depend on both the symmetric and the antisymmetric parts of $\boldsymbol{F}$.

So let's see if we can write u in a way that makes some more sense. We'll denote the line segments that connect the vertices by $d\boldsymbol{X}^{(A)}$, $d\boldsymbol{X}^{(B)}$ and $d\boldsymbol{X}^{(C)}$ and their deformed counterparts as $d\boldsymbol{x}^{(A)} = \boldsymbol{F}d\boldsymbol{X}^{(A)}$, $d\boldsymbol{x}^{(B)} = \boldsymbol{F}d\boldsymbol{X}^{(B)}$ and $d\boldsymbol{x}^{(C)} = \boldsymbol{F}d\boldsymbol{X}^{(C)}$. The deformed lengths are

$$L_\alpha^2 = d\boldsymbol{x}^{(\alpha)} \cdot d\boldsymbol{x}^{(\alpha)} = d\boldsymbol{X}^{(\alpha)T}\boldsymbol{F}^T\boldsymbol{F}d\boldsymbol{X}^{(\alpha)} = \boldsymbol{F}^T\boldsymbol{F} : \left(d\boldsymbol{X}^{(\alpha)} \otimes d\boldsymbol{X}^{(\alpha)}\right)\ . \quad (16)$$

Starting to look familiar? (I remind you of the definition of the Green-Lagrange strain tensor $\boldsymbol{E} \equiv \frac{1}{2}(\boldsymbol{F}^T\boldsymbol{F} - \boldsymbol{I})$). In order to write the energy, it seems that the matrices $\boldsymbol{M}^{(\alpha)} \equiv d\boldsymbol{X}^{(\alpha)} \otimes d\boldsymbol{X}^{(\alpha)}$ will be handy. Explicitly, they read

$$\boldsymbol{M}^{(A)} = a^2\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \quad \boldsymbol{M}^{(B)} = \frac{a^2}{4}\begin{pmatrix} 1 & \sqrt{3} \\ \sqrt{3} & 3 \end{pmatrix} \quad \boldsymbol{M}^{(C)} = \frac{a^2}{4}\begin{pmatrix} 1 & -\sqrt{3} \\ -\sqrt{3} & 3 \end{pmatrix}\ . \quad (17)$$

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[1] Since every spring is shared between two cells.

Note that $\operatorname{tr}\boldsymbol{M}^{(\alpha)} = a^2$ and $\sum \boldsymbol{M}^{(\alpha)} = \frac{3}{2}a^2\boldsymbol{I}$. We are now ready to write the energy:

$$\begin{aligned}
Su &= \frac{1}{2}k\left(L_A - a\right)^2 + \frac{1}{2}k\left(L_B - a\right)^2 + \frac{1}{2}k\left(L_C - a\right)^2 \\
&= \frac{1}{2}k\Big[L_A^2 + L_B^2 + L_C^2 - 2a(L_A + L_B + L_C) + 3a^2\Big] \\
&= \frac{1}{2}k\left[\boldsymbol{F}^T\boldsymbol{F} : \left(\sum_\alpha \boldsymbol{M}^{(\alpha)}\right) - 2a\sum_\alpha \sqrt{\boldsymbol{F}^T\boldsymbol{F} : \boldsymbol{M}^{(\alpha)}} + 3a^2\right] \\
&= \frac{1}{2}k\left[\frac{3}{2}a^2\operatorname{tr}(\boldsymbol{F}^T\boldsymbol{F}) - 2a\sum_\alpha \sqrt{\boldsymbol{F}^T\boldsymbol{F} : \boldsymbol{M}^{(\alpha)}} + 3a^2\right] \\
&= \frac{1}{2}k\left[\frac{3}{2}a^2\operatorname{tr}(2\boldsymbol{E} + \boldsymbol{I}) - 2a\sum_\alpha \sqrt{(2\boldsymbol{E} + \boldsymbol{I}) : \boldsymbol{M}^{(\alpha)}} + 3a^2\right] \Rightarrow \\
u &= k\sqrt{3}\left[\operatorname{tr}\boldsymbol{E} - \frac{2}{3}\sum_\alpha \sqrt{1 + 2\boldsymbol{E} : \tilde{\boldsymbol{M}}^{(\alpha)}} + 2\right] ,
\end{aligned} \tag{18}$$

where we defined $\tilde{\boldsymbol{M}}^{(\alpha)} = a^{-2}\boldsymbol{M}^{(\alpha)}$ and in the last transition we divided by S.

So that's about it. This is the energy function in its full glory. Two things are worth noting about this energy function: First, you can already see that it depends only on $\boldsymbol{E}$ which is rotationally invariant and symmetric. That is, the continuum level quantity $\boldsymbol{E}$ emerges naturally from the discrete analysis. Second, note that although we are using strictly linear springs whose energies are quadratic in their elongation the energy function is far from being a simple quadratic function. This is because the geometry itself introduces nonlinearities.

Let's take this one step further, and develop u in orders of $\boldsymbol{E}$ to see if we can get understand this better. The zeroth order clearly vanishes, which is a good sign that we didn't have any mistakes. The first order should also vanish (why?), and indeed

$$u^{(1)} = k\sqrt{3}\left[\operatorname{tr}\boldsymbol{E} - \frac{2}{3}\sum_\alpha\left(1 + \boldsymbol{E} : \tilde{\boldsymbol{M}}^{(\alpha)}\right) + 2\right] = k\sqrt{3}\left[\operatorname{tr}\boldsymbol{E} - \frac{2}{3}\boldsymbol{E} : \sum_\alpha \tilde{\boldsymbol{M}}^{(\alpha)}\right] = 0$$

So in all subsequent orders we can worry only about the sqrt term. To second order we have (recall that $\sqrt{1+x} \approx 1 + \frac{x}{2} - \frac{x^2}{8}$)

$$u^{(2)} = \frac{k}{\sqrt{3}}\sum_\alpha\left(\boldsymbol{E} : \tilde{\boldsymbol{M}}^{(\alpha)}\right)^2 = \frac{k}{\sqrt{3}}\sum_\alpha E_{ij}E_{kl}\tilde{M}_{ij}^{(\alpha)}\tilde{M}_{kl}^{(\alpha)} = \frac{1}{2}E_{ij}E_{kl}C_{ijkl} \tag{19}$$

$$C_{ijkl} \equiv \frac{2k}{\sqrt{3}}\sum_\alpha \tilde{M}_{ij}^{(\alpha)}\tilde{M}_{kl}^{(\alpha)} = \left(\frac{2k}{a^4\sqrt{3}}\sum_\alpha d\boldsymbol{X}^{(\alpha)} \otimes d\boldsymbol{X}^{(\alpha)} \otimes d\boldsymbol{X}^{(\alpha)} \otimes d\boldsymbol{X}^{(\alpha)}\right)_{ijkl} \tag{20}$$

$\boldsymbol{C}$ is called the stiffness tensor and you've heard a lot about it in Eran's lecture. Note that the fact that to quadratic order $u = E_{ij}E_{kl}C_{ijkl}$ for *some* tensor $\boldsymbol{C}$ is generally true in the framework of linear elasticity. Also, the fact that C_{ijkl} is symmetric under any of the transpositions $i \leftrightarrow j$, $k \leftrightarrow l$ and $ij \leftrightarrow kl$ (and any compositions of them) also generally holds. However, our $\boldsymbol{C}$ has some extra symmetries on top of that. First, note that

$C_{ikjl} \propto \sum_\alpha dX_i^{(\alpha)} dX_j^{(\alpha)} dX_k^{(\alpha)} dX_l^{(\alpha)}$ so the tensor is fully symmetric to any permutation of $ijkl$. But there's even more than that: In fact, explicit calculation shows that

$$C_{ijkl} = \frac{\sqrt{3}}{4} k \Big(\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{kj} \Big) \ , \tag{21}$$

which is, pretty surprisingly, an *isotropic tensor*. That is, to leading order the elastic response of triangular lattice is isotropic, although the lattice is clearly not invariant to rotations. Explicitly, we have

$$u(\boldsymbol{E}) = \frac{\sqrt{3}k}{8} E_{ij}E_{kl} \Big(\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{kj} \Big) = \frac{\sqrt{3}}{8} k \Big((\mathrm{tr}\, \boldsymbol{E})^2 + 2\, \mathrm{tr}(\boldsymbol{E}^2) \Big) \ . \tag{22}$$

As explained at length by Eran last week, the relation between the stress and the strain is $\boldsymbol{\sigma} = \frac{\partial u}{\partial \boldsymbol{\varepsilon}} = C_{ijkl}\varepsilon_{kl}$ (note that I switched from $\boldsymbol{E}$ to $\boldsymbol{\varepsilon}$, which is OK because we're in the linear approximation within which the two are identical). Thus,

$$\begin{aligned} \sigma_{ij}(\boldsymbol{\varepsilon}) &= \frac{\sqrt{3}k}{4} \varepsilon_{kl} \Big(\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{kj} \Big) = \frac{\sqrt{3}k}{4} \Big(\delta_{ij}\, \mathrm{tr}\, \boldsymbol{\varepsilon} + 2\varepsilon_{ij} \Big) \ , \\ \boldsymbol{\sigma} &= \frac{\sqrt{3}k}{2} (\mathrm{tr}\, \boldsymbol{\varepsilon}) \boldsymbol{I} + \frac{\sqrt{3}k}{4} \boldsymbol{\varepsilon} \ , \end{aligned} \tag{23}$$

As you'll see next week, the form $\boldsymbol{\sigma} = \lambda (\mathrm{tr}\, \boldsymbol{\varepsilon}) \boldsymbol{I} + 2\mu \boldsymbol{\varepsilon}$ for two constants λ, μ is the most general constitutive relation for linear isotropic materials. λ and μ are called Lamé coefficients (μ is also called the shear modulus). Note that the microscopic lengthscale a does not appear explicitly in the theory, a common situation in continuum theories (but if we were to include also strain-gradient terms, we could not have avoided having a in our equations).

4 Onsager's reciprocal relations

We have talked in class about the continuum description of the laws of thermodynamics. As a complementary discussion, we present here the notion of Onsager's Reciprocal Relations, a fundamental concept in close-to-equilibrium statistical mechanics. Though this is not directly related to continuum theory (i.e. they do not involve spatial degrees of freedom), they are crucial in understanding macroscopic response of thermodynamic systems, and we feel that no introductory course in non-equilibrium thermodynamics can be complete without it. These relations are derived within a linear response theory, i.e. close to thermal equilibrium. This is the simplest non-equilibrium case and later in the course we'll go nonlinear, which will be a whole lot of fun.

4.1 Transport coefficients (out of eq. properties)

Say there is a set of thermodynamic variables $\{A_i\}$ that describe our system. For simplicity we'll assume that $\langle A_i \rangle = 0$, otherwise we can always define $\alpha_i = A_i - \langle A_i \rangle$. We define the conjugate fluxes and forces to be

$$J_i \equiv \frac{dA_i}{dt} \ , \qquad\qquad X_i \equiv \frac{\partial S}{\partial A_i} \ , \tag{24}$$

where S is the system's entropy (but could equally as well be any thermodynamic potential). Note that by J_i we mean a steady change in A_i, not thermal fluctuations. These changes are maintained by fixing the forces X_i. Using (24), we can write the entropy production rate Σ as

$$\Sigma = \frac{dS}{dt} = \sum_i J_i X_i \tag{25}$$

The basic assumption of close-to-equilibrium thermodynamics is that the fluxes are linear functions of the forces. This is known by the name *linear response*. Explicitly, we write

$$J_i = \sum_j L_{ij} X_j \ . \tag{26}$$

The matrix L_{ij} is called the transport matrix, or the conductivity matrix. The meaning of "linear response" is that the coefficients L_{ij} *do not depend on* X_i. They may depend on state variables such as the temperature, but not on the forces.

Plugging (26) into (25) gives

$$\Sigma = \sum_{i,j} L_{ij} X_i X_j \ . \tag{27}$$

The 2^{nd} law of thermodynamics tells us that Σ is non-negative. We therefore see immediately that L_{ij} is a positive-definite matrix. This constraints the transport coefficient in a strong way. For example, for any pair of indices i, j we must have

$$L_{ii},\ L_{jj} < 0 \tag{28}$$

$$\det \begin{pmatrix} L_{ii} & L_{ij} \\ L_{ji} & L_{jj} \end{pmatrix} = L_{ii}L_{jj} - L_{ij}L_{ji} < 0 \ . \tag{29}$$

But Onsager tells us even more, with further reasoning that goes beyond the 2^{nd} law.

4.2 Equilibrium properties

For Onsager's relation to hold, we need to assume microscopic time-reversibility. Thus, the equilibrium correlations must satisfy

$$C_{ij}(\tau) = \langle A_i(t) A_j(t+\tau) \rangle = \langle A_i(t) A_j(t-\tau) \rangle = C_{ij}(-\tau) \ . \tag{30}$$

Also, in equilibrium we have stationarity so we can shift the time by τ and get

$$\langle A_i(t) A_j(t+\tau) \rangle = \langle A_i(t+\tau) A_j(t) \rangle \ . \tag{31}$$

Close to equilibrium, we can approximate that

$$S = S_{eq} + \Delta S(A_1, \ldots, A_n) \approx S_{eq} - \frac{1}{2} \sum_{i,j} g_{ij} A_i A_j \ , \qquad g_{ij} \equiv -\frac{\partial^2 S}{\partial A_i \partial A_j} \ . \tag{32}$$

The linear term vanishes because in equilibrium S is maximal, and the minus sign makes g_{ij} positive definite. g_{ij} is also clearly symmetric. In particular, we see that

$$X_i = \frac{\partial S}{\partial A_i} = \frac{\partial \Delta S}{\partial A_i} \approx -\sum_j g_{ij} A_j \tag{33}$$

From the definition of the entropy, the probability measure for fluctuations is

$$f(A_1, \ldots, A_n) = e^{S(A_1,\ldots,A_n)/k_B} \approx \frac{e^{\Delta S(A_1,\ldots,A_n)/k_B}}{\text{normalization}} \tag{34}$$

The matrix g_{ij} quantifies the fluctuations in the system - one can immediately calculate the instantaneous correlation $\langle A_i A_j \rangle$ by simple Gaussian integration with the measure f. However, it does not tell us anything about dynamics.

Eq. (34) tells us that

$$\log(f) = -\frac{1}{2k_B} g_{ij} A_i A_j + const \tag{35}$$

$$k_B \frac{\partial \log f}{\partial A_i} = -g_{ij} A_j = X_i \tag{36}$$

We therefore get the orthogonality criterion:

$$\begin{aligned} \langle A_i X_j \rangle &= \int A_i X_j f(A_1, \ldots, A_n) dA_1 \ldots dA_n \\ &= k_B \int A_i \frac{\partial \log f}{\partial A_j} f dA_1 \ldots dA_n = k_B \int A_i \frac{\partial f}{\partial A_j} dA_1 \ldots dA_n \\ &= k_B \int \left(\frac{\partial}{\partial A_j}(A_i f) - f \frac{\partial A_i}{\partial A_j} \right) dA_1 \ldots dA_n = -k_B \delta_{ij} \ . \end{aligned} \tag{37}$$

The first term vanishes as it is a boundary term, and the second term is δ_{ij} because f is normalized and $\{A_i\}$ are independent.

4.3 The regression hypothesis and symmetry of L_{ij}

Eq. (26) describes the dynamics of equilibrium fluctuations of $\{A_i\}$. Onsager assumed that when we take the system out of equilibrium by applying external forces, the dynamics will still be governed by Eq. (26), although the Hamiltonian has changed. That is, Onsager assumed that the relaxation ("regression") towards equilibrium follows the same dynamics as equilibrium fluctuations do. This is called "the regression hypothesis". We therefore have

$$J_i(t) = \sum_j L_{ij} X_j(t) \tag{38}$$

With this at hand, we can differentiate Eq. (31) with respect to τ. The LHS gives

$$\frac{\partial}{\partial \tau} \langle A_i(t) A_j(t+\tau) \rangle |_{\tau=0} = \langle A_i(t) J_j(t) \rangle = \sum_k \langle A_i(t) L_{jk} X_k(t) \rangle = -k_B \sum_k L_{jk} \delta_{ik} = L_{ji} \tag{39}$$

Where we used Eq. (37) to obtain the δ. Similarly, the RHS gives

$$\frac{\partial}{\partial\tau}\left\langle A_i(t+\tau)A_j(t)\right\rangle|_{\tau=0} = \left\langle J_i(t)A_j(t)\right\rangle = \sum_k \left\langle L_{ik}X_k(t)A_j(t)\right\rangle = -k_B\sum_k L_{ik}\delta_{kj} = L_{ij} \tag{40}$$

Equating (39) and (40) gives the famous Onsager Reciprocal Relations:

$$L_{ij} = L_{ji} \tag{41}$$

4.4 Remarks

4.4.1 Assumptions

Note that we needed:

- Time reversibility.
- Regression hypothesis.
- Independece of A_i, and conjugacy of A_i to J_i through ΔS.
- Linearity.

4.5 Relaxation to equilibrium

Why do systems relax toward equilibrium? One can see this by using Onsager Relations, as we will now show. Since g_{ij} is symmetric positive definite, we can choose to work with rotated and scaled variables A_i' for which $g_{ij} = \delta_{ij}$. Thus, the relation (33) takes the simple form $X_i = -A_i$. The evolution of A_i is then

$$\partial_t A_i = J_i = \sum_j L_{ij}X_j = -\sum_j L_{ij}A_j\ , \tag{42}$$

or, in compact form,

$$\partial_t\vec{A} = -\boldsymbol{L}\vec{A} \tag{43}$$

Since L_{ij} is positive definite (by the 2^{nd} law) we see that all the eigenvalues of L_{ij} have positive real parts, and therefore the system cannot explode, but we are not guaranteed that we'll have decay towards equilibrium ($\vec{A} = 0$). Onsager tells us that since L_{ij} is symmetric, it is diagonalizable with real eigenvalues, and therefore must decay towards equilibrium without oscillations. For example, suppose we had

$$\boldsymbol{L} = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \tag{44}$$

This $\boldsymbol{L}$ does not violate the 2^{nd} law, but what will the dynamics look like? Let's say we start with the initial condition $A_1 = 1,\ A_2 = 0$. The solution of the ODE (43) is

$$\begin{pmatrix} A_1(t) \\ A_2(t) \end{pmatrix} = \exp\left[\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} t\right]\begin{pmatrix} A_1(t=0) \\ A_2(t=0) \end{pmatrix} = \begin{pmatrix} \cos t & -\sin t \\ \sin t & \cos t \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} \cos t \\ \sin t \end{pmatrix} \tag{45}$$

The solutions are oscillatory and do not decay towards equilibrium. This is because the eigenvalues of $\boldsymbol{L}$ are $\pm i$, which could not have been the case if $\boldsymbol{L}$ were symmetric.