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## Thermodynamics with internal variables

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The discussion of visco-elasticity provides a framework, both mathematical and experimental, for describing the linear visco-elastic response of materials. The latter is encapsulated in response functions such as the stress relaxation modulus  $G(t)$ , the creep compliance modulus  $J(t)$  or the complex modulus  $G^*(\omega)$ . While being very useful, these functions (e.g.  $G(t)$  and  $J(t)$ , which are “memory functions”) do not reveal the physics that underlie dissipation and memory. To better account for the underlying physics one needs to identify in each systems, or class of systems, the nonequilibrium degrees of freedom that are responsible for dissipation and memory — i.e. the account for the configurational/structural changes in the material — and to write coarse-grained equation of motion for them.

This requires a new concept, that of internal state fields (“internal variables”). To see this, let us consider the viscous part of the strain rate,  $\dot{\epsilon}^{vis}$ , and write it in the form

$$\dot{\epsilon}^{vis} = \dot{\epsilon}^{vis}(\boldsymbol{\sigma}, T, \dots) . \quad (1)$$

The “...” represents the “something else”, related to the evolution of the material’s structure, which we need to account for in addition to conventional thermodynamic fields such as  $\boldsymbol{\sigma}$  and  $T$ . We replace the “...” by a (small) set of coarse-grained internal variables/field, which describe the structural state of the material and are a generalization of “order parameters” in equilibrium statistical thermodynamics. Formally, we denote the set of these internal variables by  $\{\Lambda_\alpha\}$  and rewrite the above equation as

$$\dot{\epsilon}^{vis} = \dot{\epsilon}^{vis}(\boldsymbol{\sigma}, T, \{\Lambda_\alpha\}) . \quad (2)$$

Obviously a macroscopic system contains an extensive number of structural degrees of freedom. How then do we choose a *small* set of state variables? How do we coarse-grain? How do we derive evolution equations for the internal variables? How do we self-consistently integrate these internal variables into thermodynamics?

Instead of developing a general (and rather abstract) formalism that addresses these questions, we will follow here another path in which we develop these ideas following a concrete example. The example concerns the volume deformation of a material, which contains both elastic and dissipative parts, and is assumed to be macroscopically homogeneous (i.e. we neglect spatial gradients etc.). Such volume deformation is visco-elastic, and hence will complement and extend the discussion in the previous part of the course. The example is sufficiently generic to be relevant for the discussion of plastic deformation in the next part of the course. It is also simple enough to work out all of the details without mathematical complications and will teach us a lot.

The first step would be to decompose the elastic and viscous/dissipative parts of the rate of deformation as done in the Maxwell model

$$\dot{V} = \dot{V}^{el} + \dot{V}^{vis} . \quad (3)$$

Obviously the viscous/dissipative rate of deformation may depend on the pressure  $p$  and the temperature  $T$ . However, our main focus here is on internal variables, so we would like to ask ourselves how to relate irreversible volume deformation to the material’s

structure (the elastic part is of course described as usual by the bulk modulus and the thermal expansion coefficient). A natural assumption would be that irreversible volume deformation is mediated by the formation and annihilation of vacancies. A vacancy carries a “unit” of irreversible volume deformation of magnitude  $v_0$ . Therefore,  $\dot{V}^{vis}$  can be written as

$$\dot{V}^{vis}(p, T, N_v) = \dot{V}^{vis} = v_0 \dot{N}_v , \quad (4)$$

where  $N_v$  is the number of vacancies and serves as our internal variable. Note that  $N_v$  is a dynamical variable that satisfies its own equation of motion. In addition, as  $N_v$  is a non-equilibrium thermodynamic variable that represents a macroscopic number of degrees of freedom, we should associate with it energy and entropy.

The next step would be to write down the laws of thermodynamics as

$$\dot{U} + \dot{U}_R = -p\dot{V} , \quad (5)$$

$$\dot{S} + \dot{S}_R \geq 0 . \quad (6)$$

Our system experiences a pressure  $p$  and is coupled to a thermal reservoir of temperature  $T_R$ . The reservoir degrees of freedom are denoted by the subscript  $R$ .

At this point we should discuss the entropy of the system  $S$ . Why does it deserve a special attention? The point is that the internal variable  $N_v$  may fall out of equilibrium with the applied pressure  $p$  and temperature  $T$ , and hence  $S$  should in fact be a non-equilibrium entropy. We define  $S$  as

$$S(U, V^{el}, N_v) = k_B \log \Omega(U, V^{el}, N_v), \quad (7)$$

where  $\Omega(U, V^{el}, N_v)$  is a constrained measure of the number of states of the system with energy  $U$ , elastic volume  $V^{el}$ , and a specified value of the internal variable  $N_v$ .  $N_v$  is out of equilibrium if its value is not the one that maximizes  $S$ . When it does maximize  $S$ , i.e. when  $N_v = N_v^{eq}$ , then we require that the equilibrium entropy  $S_{eq}(U, V) = k_B \log \Omega(U, V)$  be accurately approximated by

$$\frac{1}{V} S_{eq}(U, V) \approx \frac{1}{V} S(U, V, N_v^{eq}). \quad (8)$$

This approximation must become an equality in the thermodynamic limit,  $V \rightarrow \infty$ . Note also that once  $N_v$  equilibrates, we no longer distinguish between the total volume and its elastic and viscous parts.

Next, we invert the entropy in favor of the internal energy  $S(U, V^{el}, N_v) \rightarrow U(S, V^{el}, N_v)$  and as usual have

$$\left( \frac{\partial U}{\partial S} \right)_{V^{el}, N_v} = T , \quad \left( \frac{\partial U}{\partial V^{el}} \right)_{S, N_v} = -p. \quad (9)$$

Therefore,

$$\dot{U} = -p \dot{V}^{el} + \left( \frac{\partial U}{\partial N_v} \right)_{S, V^{el}} \dot{N}_v + T \dot{S} . \quad (10)$$

The first law then becomes

$$-p \dot{V}^{vis} - \left( \frac{\partial U}{\partial N_v} \right)_{S, V^{el}} \dot{N}_v - \dot{U}_R = T \dot{S}, \quad (11)$$

where we have used  $\dot{V} = \dot{V}^{el} + \dot{V}^{vis}$  to eliminate  $\dot{V}^{el}$ . The quantity

$$W \equiv -p \dot{V}^{vis} - \left( \frac{\partial U}{\partial N_v} \right)_{S, V^{el}} \dot{N}_v, \quad (12)$$

is an important one. It quantifies the difference between the dissipative work and the rate of internal energy stored in the internal variable  $N_v$ , termed “the stored energy of cold work”.

We then isolate  $\dot{S}$  in the above version of the first law,  $\dot{S} = (W - \dot{U}_R)/T$ , and insert it into the second law to obtain

$$W - \left( 1 - \frac{T}{T_R} \right) \dot{U}_R \geq 0, \quad (13)$$

where we used  $\dot{S}_R = \dot{U}_R/T_R$  (i.e. the bath is assumed to be a “simple fluid” characterized by an internal energy of the form  $U_R(S_R)$ , or alternatively by  $S_R(U_R)$ ). Since we can vary the reservoir energy  $U_R$  independently of  $N_v$  (which controls  $W$ ), we can split the inequality above into two independent inequalities of the form

$$W = -p \dot{V}^{vis} - \left( \frac{\partial U}{\partial N_v} \right)_{S, V^{el}} \dot{N}_v \geq 0, \quad (14)$$

and

$$- \left( 1 - \frac{T}{T_R} \right) \dot{U}_R \geq 0. \quad (15)$$

The first inequality stresses again that not all of the viscous power  $-p \dot{V}^{vis}$  is dissipated, i.e. that part of it is stored in the structural degrees of freedom which evolve with irreversible deformation. The second inequality is satisfied by requiring that  $\dot{U}_R$  be a function of  $T$  that changes sign only when  $T = T_R$ ; therefore we write

$$-\dot{U}_R = A(T_R - T) \equiv Q, \quad (16)$$

where  $A \geq 0$  and  $Q$  is the rate at which heat is flowing into the system from the reservoir. It is important to understand that even if we make the common assumption of very strong heat coupling between the reservoir and the system,  $A \rightarrow \infty$ ,  $Q$  remains finite. This simply means that in this limit  $T \rightarrow T_R$  (as we expect) such that the product  $A(T_R - T)$  is finite. Note also that Eq. (16) involves an equality, not an inequality. With this definition of  $Q$ , Eq. (11) becomes

$$C_v \dot{T} \simeq T \dot{S} = W + Q = W + A(T_R - T), \quad (17)$$

where  $C_v$  is the heat capacity. This is a heat equation, which is driven by two terms. One is the coupling to the heat reservoir, which tends to equilibrate  $T$  with  $T_R$ . The strength of the coupling is  $A \geq 0$  (we usually assume this coupling to be large). The other is the dissipation associated with viscous deformation, which is a source term that tends to heat the system. This is a very general result (in a spatially varying situation an additional diffusion term would appear as well).

Our next and important task is to calculate the dissipation term  $W$ . For that aim, we need to associate energy and entropy with the internal variable  $N_v$ . We then write

$$U(S, V^{el}, N_v) = U_0(N_v) + U_1(S_1) + U_{el}(V^{el}) = e_0 N_v + U_1[S - S_0(N_v)] + U_{el}(V^{el}). \quad (18)$$

Here  $U_0(N_v)$  is the energy of the vacancies,  $e_0$  is the formation energy of a vacancy,  $S_0(N_v)$  is the entropy of the vacancies  $U_{el}(V_{el})$  is the elastic energy, and  $S_1$  and  $U_1$  are, respectively, the entropy and energy of all of the other degrees of freedom in the system. Equivalently, we can invert this relation and write it as an expression for entropy  $S$

$$S(U, V^{el}, N_v) = S_0(N_v) + S_1(U_1) = S_0(N_v) + S_1[U - e_0 N_v - U_{el}(V^{el})]. \quad (19)$$

The structure of these relations, i.e. the arguments of  $U_1$  and  $S_1$  in their second versions, describes the way the energy and entropy are shared between the vacancies and the other degrees of freedom. Note that the total entropy and energy in Eqs. (18)-(19) are assumed to have very simple forms.

We then assume that the vacancy population is dilute, i.e. that  $N_v \ll N$  (where  $N$  is the number of available sites, proportional to the number of particles in the system), and therefore

$$S_0(N_v) \simeq k_B \left[ -N_v \log \left( \frac{N_v}{N} \right) + N_v \right], \quad (20)$$

which is of course extensive. (Just to remind you how to derive this result: The number of ways to distribute  $N_v$  objects among  $N$  sites is give by  $\Omega = \frac{N!}{N_v!(N-N_v)!}$ . Take the logarithm, invoke Stirling's approximation, i.e.  $\log(x!) \simeq x \log x - x$  for large  $x$ , and  $N_v \ll N$ .) Note that

$$\frac{\partial S_0}{\partial N_v} = k_B \frac{\partial}{\partial N_v} [N_v \log N - N_v \log N_v + N_v] = -k_B \log \left( \frac{N_v}{N} \right). \quad (21)$$

Finally, we are able to calculate  $W$  for which we need first to evaluate

$$\left( \frac{\partial U}{\partial N_v} \right)_{S, V^{el}} = \frac{\partial}{\partial N_v} [U_0(N_v) - T S_0(N_v)] = e_0 + k_B T \log \left( \frac{N_v}{N} \right). \quad (22)$$

This leads to

$$W = -p v_0 \dot{N}_v - \left[ e_0 + k_B T \log \left( \frac{N_v}{N} \right) \right] \dot{N}_v \equiv - \left( \frac{\partial G_v}{\partial N_v} \right)_{T, p} \dot{N}_v \geq 0, \quad (23)$$

where

$$G_v = e_0 N_v - T S_0(N_v) + p v_0 N_v \quad (24)$$

is a vacancy-related Gibbs free-energy (it has the structure " $U - TS + pV$ "). To satisfy the second law inequality in (23), we demand that both  $-\partial G_v / \partial N_v$  and  $\dot{N}_v$  change sign at the same point.  $G_v$  attains a minimum at  $N_v = N_v^{eq}$  determined by

$$\left( \frac{\partial G_v}{\partial N_v} \right)_{T, p} = 0 \implies N_v^{eq}(p, T) = N \exp \left( -\frac{e_0 + p v_0}{k_B T} \right). \quad (25)$$

The equilibrium number of vacancies is determined by the vacancy enthalpy  $e_0 + p v_0$  through a Boltzmann factor. We then conclude that  $-\partial G_v / \partial N_v$  is a monotonically decreasing function that changes sign at  $N_v^{eq}$ . The inequality in (23) is satisfied if  $\dot{N}_v$  has the same property. It is crucial to note that in principle we have not assumed any special proximity to equilibrium and hence the deviation of  $N_v$  from  $N_v^{eq}$  need not be small, going beyond linear response. However, the degree of non-linearity is a matter of physics, not of thermodynamics, and should emerge from more detailed physical considerations. For example, in the linear response regime the inequality in (23) can be satisfied by a linear relation of the form

$$\dot{N}_v = \Gamma(T, N_v) (N_v^{eq}(p, T) - N_v) \quad , \quad (26)$$

where  $\Gamma(T, N_v)$  a positive rate factor. A nonlinear model, which we do not work out here, may lead to

$$\dot{N}_v \sim -N_v \log \left( \frac{N_v}{N_v^{eq}} \right) \quad . \quad (27)$$

The point is clear: any physical model should be consistent with the inequality in (23). It is important to note that the rate factor (i.e. the proportionality factor which has the dimension of inverse time) also contains essential physics that goes beyond thermodynamics. For example, if it deviates from a constant molecular rate – it can be much smaller and actually depend by itself on  $N_v$  — we can obtain interesting “slow” dynamics.

The upshot of this analysis are the evolution equations for  $T$  and  $N_v$ . The latter can be used to obtain  $\dot{V}^{vis}$  and once a thermo-elastic energy functional is specified, the volume  $V(t)$  can be calculated for any prescribed loading  $p(t)$  and reservoir temperature  $T_R(t)$ .

The example we worked out in detail was quite simple. Usually, things are much more involved. The basic structure of the non-equilibrium thermodynamic theory, however, and the concepts discussed are rather general.