
MATERIALS AT EQUILBIUM

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1 Lecture 1: Introduction and Preliminaries

Welcome to 3.20, Materials at Equilibrium. This course is designed to provide all incoming students with a grounding in equilibrium thermodynamics. The material in this course is broadly applicable to all field of materials science and engineering and will serve you well throughout your research as a graduate student. For information related to the course, including lecture content, problem sets, exams, staff policies, and grading please refer to your course syllabus found on Stellar, or contact the professor directly at allanore@mit.edu.

1.1 Definitions

To begin our journey, we will define some frequently used terms for convenience.

1. System: Any collection of matter that can be uniquely identified and on which you can define macroscopic averages (a system is not necessarily homogeneous)
2. Environment: The complement of a system. Together, the system being studied and it's environment make up the universe.

$$[\text{environment}] = [\text{universe}] - [\text{system}] \quad (1)$$

3. Extensive Variables: Variables that scale with the system size (i.e. volume, mass, number of particles, n_e , etc.). If we bring two containers together, the volume is a sum of the individual volumes:

$$V = V_1 + V_2 \quad (2)$$

4. Intensive Variables: Variables that are independent of the system size. Intensive variables do *not* scale with system size (i.e. pressure, temperature, E-field, etc.). For example, the sum of two system's pressures is not equal to the pressure of the sum of both systems:

$$P \neq P_1 + P_2 \quad (3)$$

5. State Variables: The variables required to fully characterize a system (T, P, n, ...). These are *not* equal to the **state** of a system. However, at equilibrium, there is a one-to-one mapping between the macroscopic state of the system and the full set of state variables; the state variables fully define the macroscopic equilibrium state.
6. Boundaries: Conditions that are defined for a system. These strongly depend on the system of interest. Boundaries can have properties such as: permeable (open to mass flow, changing n), impermeable (closed to mass flow), adiabatic (closed to heat flow), diathermal (open to heat flow), rigid (constant volume), deformable, etc. The nature of the boundary defines how the system's state variables can change as it is subjected to different processes. For example, while a system with a rigid boundary is subject to possessing a constant volume during arbitrary processes, a system with

a deformable boundary will, for sufficiently slow processes, have the same pressure as its surroundings.

In thermodynamics, we will look at the transfer of energy and other extensive variables at the borders of systems as they undergo processes. Note that this approach treats the system as a black box; we have no idea what is going on microscopically inside the system. We will derive laws regarding the conservation and creation of the extensive variables. Using these laws of conservation, we will be able to define exactly how the macroscopic state of the system changes by only keeping track of what goes on at the boundaries of the system. We will then develop constitutive equations which relate changes in the thermodynamic state variables to one another during arbitrary processes. Integration of these constitutive equations is a powerful and general way to calculate changes in system processes during arbitrary processes. Last, we will use these constitutive relationships to look at a special set of processes; phase transitions, and derive laws for how the conditions under which these phase transitions should occur have to change as the boundary conditions on the system change.

1.2 Energy and Forces

What “forms” of energy do we have?

- Potential energy: Gravitational, electrostatic, etc.
- Kinetic energy: Translation, rotations, etc.

This energy can be manifest inside and outside the system. Other examples of energies are thermal energy (from heat), electromagnetic energy, and chemical energy. For 3.20, we will assume that changes in the total energy E of our system are equal to changes in the internal energy U of the system.

$$\Delta E = \Delta U \quad (4)$$

This is tantamount to neglecting changes in the translational energy of the system as a whole. We assume that U exists, that U is a function of only the extensive thermodynamic variables (U is a state variable), and that all types of energy exchange that can change the internal state of the system can be represented as work terms represent changes in U . We discuss this final assumption next.

2 Lecture 2: Heat and Work

Let's look at one form of energy transfer: work. A differential amount of work is equal to the force dotted with the displacement:

$$\delta W = \vec{F} \cdot d\vec{r} \quad (5)$$

The formalism for work is $\delta W_i = y_i dx_i$, where y_i is the force (intensive) and dx_i is the response (extensive). Combined, (y_i, x_i) is a **conjugate pair**.

2.1 Two examples of work

Example 1: Deformation of a material: The work resulting from a change in strain energy is

$$\delta W = V \bar{\bar{\sigma}} \cdot d\bar{\bar{\epsilon}} \quad (6)$$

where the double overbars indicate that σ, ϵ are tensors. To check the validity of this statement, we note that the stress σ has units of [Pa]=[N/m²], the strain ϵ is dimensionless, and volume element results in a quantity of [N·m]=[Joules]. We note that the shear stresses in this example are denoted by off-diagonals of σ ($\sigma_{12}, \sigma_{13}, \sigma_{23}$). If we consider only hydrostatic pressure, we will have $\sigma_{11} = \sigma_{22} = \sigma_{33} = -P$.

$$\begin{aligned} \delta W_{\text{pressure}} &= V \cdot (-P) d(\epsilon_{11} + \epsilon_{22} + \epsilon_{33}) \\ &= -PV(d\epsilon_{11} + d\epsilon_{22} + d\epsilon_{33}) \end{aligned} \quad (7)$$

We note that the strain is defined as $\epsilon_{11} \equiv \Delta l_1 / l_1^{\text{initial}}$, and $l_1 l_2 l_3 = V$, so we can substitute $V(d\epsilon_{11} + d\epsilon_{22} + d\epsilon_{33}) = dV$:

$$\delta W_{\text{pressure}} = -PdV \quad (8)$$

To solve these, we need an equation of state $P(V)$ or $\sigma(\epsilon)$. We also have

$$\frac{\partial \epsilon_{ij}}{\partial \sigma_{kl}} = c_{ijkl} \quad (9)$$

where c_{ijkl} is the generalized elastic compliance. If our material is isotropic, then we will see that $\frac{\partial V}{\partial P}|_T = V \cdot \beta_T$ where β_T is the isothermal compressibility - a property of the material that describes volume changes at constant temperature. Hence, using this constitutive relation, $\beta_T(P, T)$, we can define the work done upon the system.

Example 2: Electrical work on an isotropic dielectric medium: The voltage between two sides of a dielectric is given by the internal electric field and the length as $V = \mathcal{E} \cdot l$. The energy stored in this capacitor is a product of the voltage and the charge. If the charge, q , changes, we can produce a work term:

$$\delta W = V dq \quad (10)$$

Also, $q = D \cdot A$ where D , the electric displacement, is equal to $\epsilon_0 \mathcal{E} + \frac{\mathcal{P}}{A \cdot l}$. \mathcal{P} is the total polarization and it is normalized by the volume, $A \cdot l$. We can do some algebra to arrive at a new expression for this work term:

$$\begin{aligned}\delta W &= \mathcal{E} l \cdot d\left(A\left(\epsilon_0 \mathcal{E} + \frac{\mathcal{P}}{lA}\right)\right) \\ &= \mathcal{E} l A \cdot d\left(\epsilon_0 \mathcal{E} + \frac{\mathcal{P}}{lA}\right) \\ &= V \epsilon_0 \mathcal{E} d\mathcal{E} + \mathcal{E} d\mathcal{P}\end{aligned}\tag{11}$$

Note how the δW nicely separates into a response that is independent of the system and one that is determined by the material properties of the system. Some energy, $V \epsilon_0 \mathcal{E} d\mathcal{E}$, is stored even when an electric field is applied to a vacuum. We are not interested in this energy. $\mathcal{E} d\mathcal{P}$, on the other hand, is system-dependent. This is the work term appropriate to the application of an electric field to a system. You will notice some commonalities between the mechanical work terms discussed previously and the electrical work term: both products result in units of energy, and both can be written as the product of a generalized force (an intensive thermodynamic variable, P, \mathcal{E}), and a generalized displacement (an extensive thermodynamic variable, $dV, d\mathcal{P}$). These traits are common to all work terms which appear in the internal energy. This implies that changes in the internal energy can be written as a sum over orthogonal work terms:

$$dU = \sum_i y_i dx_i \tag{12}$$

where each y_i represents a generalized force, and each x_i represents a generalized displacement.

We will now discuss how we derive the form of this summation of orthogonal work terms. You might have noticed that we were careful to define the compressibility of a system, β , over a specific path. Specifically, we defined a compressibility wherein the system was held at constant temperature, β_T . This is because the compressibility is a function of the boundary conditions under which the compression takes place.¹ This concept can be generalized to all work terms: *the work done in changing an extensive variable is a function of the path along which the work takes place*. Put simply, the change in internal energy due to the work terms are path dependent. In thermodynamics, we make a distinction between path-dependent and path-independent integrals via exact differentials and inexact differentials.

- exact differentials: The integral of an exact differential path independent; it is only a function of the endpoints.
- inexact differentials: The integral of an inexact differential is path dependent; the integral depends both on the endpoints and the path to get to these two endpoints.

This is illustrated below with two examples.

¹For example, it takes more energy to compress a gas if you don't let heat flow out of the gas during the compression; the adiabatic compressibility is larger than the isothermal compressibility.

2.2 Practice with Differentials

Case 1, Exact Differentials: Consider heights as a function of position, $h(x, y)$. We will travel from some height $h_1 \rightarrow h_2$. Anytime we move downwards, we will simply gain kinetic energy. Anytime we move up a hill, we will first use any kinetic energy we have and then use some stored energy (say, from a battery). Once we have reached h_2 , we will give all our kinetic energy to the environment (say from some thermal energy dissipation, like brakes) and we will allow the environment to replenish the energy in our batteries. The change in potential energy between the two heights is ΔE_{field} and the energy of the environment, i.e. the work required to move us to this new spot, is ΔE_{system} . From conservation of energy,

$$\Delta E_{\text{system}} + \Delta E_{\text{field}} = 0 \quad (13)$$

Therefore, we can calculate the work required to move us to the new spot via integration of the differential of the gravitational energy with respect to the position (the gravitational force field):

$$\begin{aligned} \Delta E_{\text{field}} = dW &= \int \vec{F} \cdot d\vec{r} \\ &= - \int \nabla E_{\text{field}} \cdot d\vec{r} \\ &= -mg(h_2 - h_1) \end{aligned} \quad (14)$$

Ultimately, the energy change (or work required to move us) from $h_1 \rightarrow h_2$ is independent of the path taken. Hence, \vec{F} is an exact differential. Mathematicians would say that gravitational force fields are conservative vector fields. This is an equivalence; exact differentials define conservative vector fields.

Case 2, Inexact Differentials: Consider now a system where the force \vec{F} is non-conservative. The work terms associated with moving through this kind of a vector field are then inexact differentials. dissipative forces tend to make the force vector-field non-conservative, resulting in path dependence. For example, moving in a gravitational field with a constant friction term would result in:

$$\begin{aligned} \vec{F} &= -\vec{\nabla} E - f_{\text{friction}} |\vec{e}_v| \\ \int \vec{F} \delta \vec{r} &= -mg\Delta h - f L_{\text{path}} \end{aligned}$$

In thermodynamics, you can get an inexact differential for two reasons. As described above, dissipation leads to inexact differentials. A second, related way, is simply not taking into account all of the forces during your integration. Such an incomplete description will result in path-dependent integrals, even if the underlying vector field is conservative. For example, if we are moving in three dimensions and do not describe the force in the y -direction, F'_y , then we would (incorrectly) describe the work when moving in three dimensions as:

$$\delta W_{\text{incomplete}} = \delta W_x + \delta W_z = F_x dx + F_z dz$$

Consider two different paths in a conservative 3D vector field. The integrated amount of work done due to the x- and z- forces may be different between the two paths, even though the total work is the same. This results in a path dependence in the energy acquired while moving. For path #1 we might have $\int \delta W_x + \delta W_z = \int F_x dx F_z dz = 0$ whereas for path #2 we could very well have $W_x = \int F_x dx \neq 0$. This is analogous to describing the changes in internal energy of a system through only work terms; we are missing an entire component of the internal energy change, the change due to heat flow into a system.

2.3 Heat

Heat is energy transferred between two bodies not due to work or mass transfer.² The variable we will use to denote heat is Q . A system surrounded by an adiabatic boundary does not transfer heat across its boundaries, and so we say the heat exchanged between the system and the surroundings is 0; $\delta Q = 0$. The first postulate of thermodynamics is

$$\boxed{dU = \delta W + \delta Q} \quad (15)$$

The value of U is path independent via the conservation of energy. As such, U is a function of solely the system's state. Appropriately, functions which are completely defined by the thermodynamic state of the system are called state functions; their differentials must thus be exact differentials. On the contrary, W and Q are path dependent; transfer of energy can be accomplished in a multitude of ways. This is why we write both changes in heat and work with the inexact differential symbol, δ , but the sum of the two as dU .

Example: Consider a simple system with all variables fixed except for the volume, like a piston. It then evolves “slowly” through a series of equilibrium states.³

$$W = - \int P dV \quad (16)$$

Assuming we are dealing with an ideal gas, we have the following equation of state $P = \frac{nRT}{V}$. Inserting this into the above (and assuming constant temperature), we have an expression

²Historically, people used to think heat was transferred between bodies via the flow of an invisible substance, *phlogiston*. Hot bodies contained more of this self-repelling fluid than cold bodies. Two heroes of science helped disprove this crazy theory. First, Antoine Lavoisier showed that metals gained mass when they oxidized, even though they were supposed to lose phlogiston, so phlogiston would need to have negative mass. This led to phlogiston theory being replaced by caloric theory, in which calor, another invisible liquid, flowed from hot to cold bodies. All caloric theories assumed that calor was conserved. Sir Benjamin Thompson (AKA Lord Rumford) disproved this theory by showing that repeatedly boring a cannon could repeatedly produce heat, showing that heat was not a conserved quantity, but rather, could be generated. This led to Rudolf Clausius proposing that it is not heat which is conserved, but rather energy. This was the birth of modern thermodynamics.

³We call such infinitely slow processes, where in the system can be approximated as being in equilibrium the whole time quasistatic processes.

for work in terms of the initial and final volumes.

$$\begin{aligned} W &= -nRT \int \frac{dV}{V} \\ &= nRT \ln \left(\frac{V_f}{V_i} \right) \end{aligned} \tag{17}$$

It is often useful to think of these changes as paths in a pressure versus volume plot. Let's consider a path a where both the pressure and volume can change. We will compress the gas isothermally from a volume V_1 to a final volume $V_f = V_1/2$. Also, we are at room temperature, $T = 298K$.

$$\begin{aligned} W_a &= -nRT \int \frac{dV}{V} \\ &= -nRT \ln \left(\frac{V_f}{V_i} \right) \\ &= nRT \ln(2) \\ &= 1717 \frac{\text{J}}{\text{mol}} \end{aligned} \tag{18}$$

Let's now consider a separate path b that is first isobarically compressed ($dP = 0$), and then isochorically warmed ($dV = 0$), such that both the initial and final states are the same as those in a . For the constant volume pressure change, there will be no work done since $dV = 0$ and $W = -PdV$. Therefore all the work will come from the initial constant pressure process, or isobaric compression.

$$\begin{aligned} W_b &= -P_i \int dV \\ &= \frac{P_i V_i}{2} \\ &= \frac{nRT}{2} \\ &= 1239 \frac{\text{J}}{\text{mol}} \end{aligned}$$

Clearly, the amount of work done when changing between two states can be different, although the change in internal energy must be the same. Thus, there must have been different amounts of heat transferred along each path as well; both work and heat are path-dependent.