
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, 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 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.
6. Boundaries: Conditions that are defined for a system. These strongly depend on the system of interest. A boundary might describe if a system is permeable (open to matter, changing n), closed (closed to matter), adiabatic (lack of heat flow), athermal (no heat flow), rigid (non-deformable), deformable, etc. They can speak about extensive variables and limit/confine the system.

In 3.20 we will look at the transfer of energy at the borders. Inside the system we have state variables (T, P, n, etc.) and we will ultimately create constitutive equations so that we may calculate unknowns.

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 the change in internal energy U .

$$\Delta E = \Delta U \tag{4}$$

We assume that U exists and it is a state variable that represents all types of energy exchange that can change the internal states of the system.

2 Lecture 2: Heat and Work

Let's look at one form of energy transfer: work, which is equal to the force times the displacement.

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

The formalism for work is $\partial W_i = y_i dx_i$, 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

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

where the double overbars denote σ, ϵ are tensors. To check the validity of this statement, we note that the stress σ has units of $[\text{Pa}] = [\text{N}/\text{m}^2]$, the strain ϵ is dimensionless, and volume element results in a quantity of $[\text{N} \cdot \text{m}] = [\text{Joules}]$. 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 $\sigma_{11} = \sigma_{22} = \sigma_{33} = -P$.

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

We note that the strain is defined as $\epsilon_{11} \equiv \Delta l_1 / l_1^{(0)}$, and $l_1 l_2 l_3 = V$, so we can substitute $V d\epsilon_{11} d\epsilon_{22} d\epsilon_{33} = dV$:

$$\partial W_{\text{pressure}} = -P dV \quad (8)$$

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 constant. 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.

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 $V = E \cdot l$. The energy stored in this capacitor is a product of the voltage and the charge. If the charge 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 $\epsilon_0 E + \frac{P}{A \cdot l}$. P is the total polarization and it is normalized by the volume.

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

Next, we can relate this quantity to the characteristic potential energy function of our system. We know that $\Delta U = U^{\text{final}} - U^{\text{initial}}$, and $\partial W = y_i dx_i = F d\vec{r}$. The force from a potential energy function ϕ is $\vec{F}(\vec{r}) = -\vec{\nabla}\phi(\vec{r})$. Therefore, we have

$$\begin{aligned}F_x &= -\frac{\partial\phi}{\partial x}|_y \\ F_y &= -\frac{\partial\phi}{\partial y}|_x\end{aligned}$$

$\vec{F}d\vec{r}$ is an exact differential. It's integral is path independent. $\oint \vec{F} \cdot d\vec{r} = 0$. Also, \vec{F} is a conservative force. It is like the “vehicle” that converts gravitational energy, E_g to electricity.

$$\begin{aligned}\int_{r_1}^{r_2} \vec{F} d\vec{r} &= \int -\vec{\nabla}\phi(\vec{r}) d\vec{r} \\ &= [\phi(\vec{r}_2) - \phi(\vec{r}_1)]\end{aligned}$$

2.2 Practice with Differentials

Case 1, Exact Differentials: Consider a contour of heights $h(x, y)$. 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,

$$\Delta E_{\text{system}} + \Delta E_{\text{field}} = 0\tag{12}$$

Therefore, we can calculate the work required to move us to the new spot:

$$\begin{aligned}\Delta E_{\text{field}} &= dW = \int \vec{F} \cdot d\vec{r} \\ &= - \int \nabla E_{\text{field}} \cdot d\vec{r} \\ &= -mg(h_2 - h_1)\end{aligned}\tag{13}$$

Ultimately, the energy change (or work required to move us) from $h_1 \rightarrow h_2$ is independent of the path taken. This property manifests itself in the nature of the conservative vector field F . The change in work may then be expressed as an exact differential.

Case 2, Inexact Differentials: Consider now a system where the force F is non-conservative. The energy associated with moving through this kind of a vector field must then be described by an inexact differential. For example, if we are missing a force, say F'_y , then the change in work when moving in three dimensions is:

$$\delta W_{\text{new}} = \delta W_x + \delta W_z$$

Consider two different paths. The amount of work done along the x-direction may be different between the two. However, there is no work associated with moving along the y-direction connecting the two paths. This results in a path dependence in the energy acquired while moving. For path #1 we might have $\int \partial W_x = \int F_x dx = 0$ whereas for path #2 we could very well have $W_x = \int F_x dx \neq 0$.

Additionally, dissipative forces tend to make the force vector-field non-conservative, resulting in path dependence.

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

2.3 Heat

Heat is energy transferred between two bodies. This is strictly different from work and mass transfer. The variable we will use to denote heat is Q . A system that is adiabatic does not transfer heat, and so we say $\partial Q = 0$. The first postulate of thermodynamics is

$$\boxed{dU = \partial W + \partial Q} \quad (14)$$

U is a property of a system - a function of the system's state. On the contrary, W and Q are not (they refer to a transfer of energy). Thompson (Rumford) measured mass change with varying temperature in water to help observe this phenomena.

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, and so we say it evolves quasistatically.

$$W = - \int P dV \quad (15)$$

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 for work in terms of the initial and final volumes.

$$\begin{aligned}W &= -nRT \int \frac{dV}{V} \\ &= nRT \ln \left(\frac{V_f}{V_i} \right)\end{aligned} \quad (16)$$

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, $T = 298K$.

$$\begin{aligned}
 W_a &= -nRT \int \frac{dV}{V} \\
 &= -nRT \ln\left(\frac{V_f}{V_i}\right) \\
 &= nRT \ln(2) \\
 &= 1717 \frac{\text{J}}{\text{mol}}
 \end{aligned} \tag{17}$$

Let's now consider a separate path b that is first isobarically compressed ($dP = 0$), and then isochorically compressed ($dV = 0$), such that the final state is the same as the final state from path 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.

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