PHYS 213 UIUC Notes

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Contents

The majority of these notes are taken from the course textbook [2]. There are wonderful prelecture notes that summarize them. This is a summary of those notes.

1 Equilibrium

This section covers the first 3 weeks of the class. With the grounding definitions, such as that of macro/microstates, entropy, and that of quasistatic processes, we begin to explain what thermodynamics is.

Following the law that all energy is conserved, in Thermodynamics, we split these energy into mechanical and internal. These are related by the First Law of Thermodynamics,

Theorem 1 (1^{st} Law)**.** *Heat is divided between internal energy and work*

$$\mathrm{d}Q = \mathrm{d}U - p\,\mathrm{d}V$$

Each variable in this equation are what we call *macrovariables.* These quantities are things that we may observe.

On the contrary, we have the notion of *microstates.* That is, let Ω be the number of configurations that may form the same macroscopic state. Then, we define entropy to be macrostates that encompasses microstates, by

Definition 1 (Entropy)**.**

$$S \equiv k_B \ln \Omega$$

Now, we begin to talk about equilibrium conditions. Intuitively, the equilibrium state is that which is the most probable. That is, because of the *central limit theorem* and the *law of large numbers*, it is much more probable to be in one of the states that maximize S than one that doesn't.

Putting this together with an example, consider the following "two-bricks" model. Let blocks A and B be a closed system, with entropies $S_A(U_A)$ and $S_B(U_B)$ respectively. Further, let $U = U_A + U_B$, so that $\mathrm{d}U_A = -\mathrm{d}U_B$. Since we want to maximize entropy, we take the derivative

$$\begin{aligned}\frac{\partial S_{\text{TOT}}}{\partial S(U_A)} = 0 &= \frac{\partial S(U_A)}{\partial U_A} + \frac{\partial S(U_B)}{\partial U_A} \\ &= \frac{\partial S(U_A)}{\partial U_A} - \frac{\partial S(U_B)}{\partial U_B}\end{aligned}$$

so we have the following definition that matches temperature with this notion of equilibrium,

Definition 2 (Temperature)**.**

$$T \equiv \frac{\partial S}{\partial U}$$

Similarly, in such a state with equal temperatures, we also expect pressure to be the same. In a model with volumes $V = V_A + V_B$,

$$\begin{aligned}\frac{\partial S_{\text{TOT}}}{\partial S(V_A)} = 0 &= \frac{\partial S(V_A)}{\partial V_A} + \frac{\partial S(V_B)}{\partial V_A} \\ &= \frac{\partial S(V_A)}{\partial V_A} - \frac{\partial S(V_B)}{\partial V_B}\end{aligned}$$

so we have the following definition of pressure,

Definition 3 (Pressure)**.**

$$\frac{p}{T} \equiv \frac{\partial S}{\partial V}$$

The last definition is the notion of chemical potential. In a model with number $N = N_A + N_B$,

$$\begin{aligned}\frac{\partial S_{\text{TOT}}}{\partial S(N_A)} = 0 &= \frac{\partial S(N_A)}{\partial N_A} + \frac{\partial S(N_B)}{\partial N_A} \\ &= \frac{\partial S(N_A)}{\partial N_A} - \frac{\partial S(N_B)}{\partial N_B}\end{aligned}$$

so we have the following definition of potential,

Definition 4 (Chemical Potential)**.**

$$\frac{\mu}{T} \equiv -\frac{\partial S}{\partial N}$$

Using these three definitions, we can see the relationship between the macrostates

Theorem 2 (Fundamental Relation)**.**

$$\mathrm{d}S = \frac{1}{T}\,\mathrm{d}U + \frac{p}{T}\,\mathrm{d}V - \frac{\mu}{T}\,\mathrm{d}N = \frac{\mathrm{d}Q}{T}$$

Proof. With 6 macrostates S, U, V, N, p, T, we notice that only 4 of them are necessary to describe a system. That is, since p and T are determined by the derivatives of S, we can omit them.

$$\begin{aligned}\frac{\partial S(U,V,N)}{\partial t} &= \frac{\partial S}{\partial U}\frac{\partial U}{\partial t} + \frac{\partial S}{\partial V}\frac{\partial V}{\partial t} + \frac{\partial S}{\partial N}\frac{\partial N}{\partial t} \\ &= \frac{1}{T}\frac{\partial U}{\partial t} + \frac{p}{T}\frac{\partial V}{\partial t} - \frac{\partial \mu}{\partial T}\frac{\partial N}{\partial t}\end{aligned}$$

□

2 Kinetic Theory of Gasses

We apply our abstract definitions in one of the recurring systems of the course — that of the ideal gas. Under the assumptions that particles do not interact, our model gives us that

$$\Omega(U,V,N) = \Omega(U,V,1)^N = (g(U)V)^N$$

for some unknown function g.
Thus, we may calculate the entropy of a system of ideal gas to be

$$\begin{aligned}\frac{\partial S}{\partial V} &= \frac{p}{T} \\ &= Nk_B \frac{\partial}{\partial V} \ln g(U)V = Nk_B V\end{aligned}$$

Rearranging, this provides us with the familiar relation

Equation 1 (Ideal Gas Law)**.**

$$pV = Nk_BT$$

Analyzing this classically, in particular a gas inside a box, we can calculate the force of particles using Newton's 2nd law

$$F \equiv \frac{\mathrm{d}(mv)}{\mathrm{d}t}$$

In particular, for an individual face of the cube, we have collisions imparting a change in momentum of $2mv$ which happen every $2d/v$ time, leading to an average pressure of

$$p = \frac{F}{A} = \frac{2mv}{2d/v \cdot d^2} = \frac{mv^2}{V}$$

For 3 spacial dimensions, recalling that $U = \langle K \rangle_{trans} = \frac{1}{2}mv^2$,

$$pV = Nk_BT = \frac{Nm\langle v \rangle^2}{3} = \left(\frac{2N}{3}\right)U$$

and in other words, that

Equation 2.

$$U = \frac{3}{2}k_BT$$

This is a special case of a more general phenomena of equipartition of heat. That is,

$$U = \frac{N_{\text{DOF}}}{2}k_BT$$

Thus, with the following definition,

Definition 5 (Heat Capacity)**.**

$$C = \frac{\partial U}{\partial T}$$

Theorem 3 (Equipartition)**.**

$$C_V = \frac{N_{\text{DOF}}}{2} k_B$$

Equipartition is fundamentally a quantum effect, and it is not always the most precise. For this course, we need to remember that diatomic atoms have 2 rotational degrees of freedoms, and up to 7 at high temperatures (2 vibrational modes). Similarly, solids always have 6 degrees of freedom.

Finally, when equipartition applies, it is often useful to calculate the change in entropy as

Equation 3.

$$\Delta S = \int \frac{C}{T} \, \mathrm{d}T$$

by using the fundamental relation $\mathrm{d}S = \frac{\mathrm{d}Q}{T}$ and applying a change of variables.

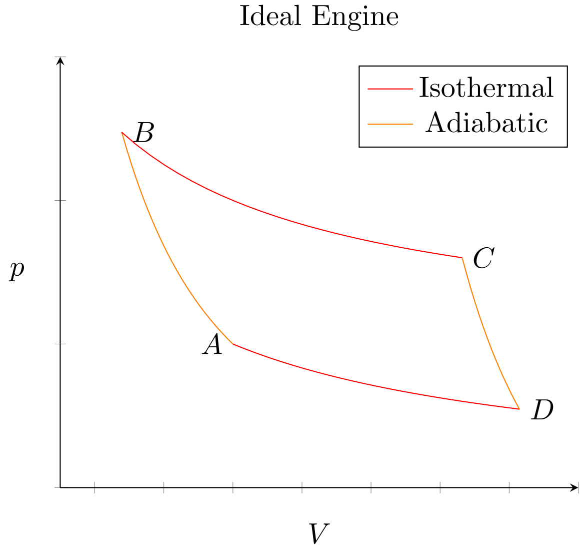
3 Thermodynamic Processes

Now, we practice making use of all these macrostate variables to model the different evolutions for quasi-static processes. These are processes such that at all times, we stay in equilibrium — hence the name quasi-static. In particular, those of fixed pressure (isobaric), temperature (isothermal), volume (isochoric), and energy (adiabatic). Then, we discuss how to develop sustainable cycles that maximize work (engines, heat pumps).

Theorem 4 (2^{nd} Law)**.** *For any thermodynamic process,*

$$\Delta S = \int_{S_i}^{S_f} \mathrm{d}S \geq 0$$

We consider the example of an ideal engine, studying the effects of isothermal and adiabatic processes.



Cycling between isothermal and adiabatic processes, we go clockwise in this diagram.
First, from $A \to B$, we first do an adiabatic compression. That is, we heat the gas to increase the pressure, allowing volume to change but not allowing any heat to escape.
Deriving the pressure-volume relationship for an ideal gas in an adiabatic process,

$$\begin{aligned} Nk_B\,\mathrm{d}T &= \frac{2\,\mathrm{d}U}{N_{\text{DOF}}} && \text{(equipartition)} \\ &= -\frac{2p\,\mathrm{d}V}{N_{\text{DOF}}} && \text{(1st Law)} \\ &= p\,\mathrm{d}V + V\,\mathrm{d}p && \text{(Ideal Gas)} \end{aligned}$$

Solving algebraically,

$$p\left(\frac{2}{N_{\text{DOF}}}+1\right)\mathrm{d}V+V\,\mathrm{d}p=0$$

and defining $\gamma=\frac{2}{N_{\text{DOF}}}+1$, dividing both sides by p

$$\begin{aligned}C&=\int\frac{\gamma}{V}\,\mathrm{d}V+\int\frac{\mathrm{d}p}{p}\\&=\gamma\ln V+\ln p\\&=\ln pV^{\gamma}\end{aligned}$$

and finally, for an ideal gas in adiabatic equilibrium,

Equation 4.

$$pV^{\gamma}\equiv\mathit{constant}$$

In other words,

$$\frac{p_A}{p_B}=\frac{V_B^{\gamma}}{V_A^{\gamma}}$$

Since we are in a closed system, there is no heat transfer, and thus no entropy change. However, in heating the gas, we are putting in work and increasing its internal energy, so that

$$W_{applied}=-\int p\,\mathrm{d}V>0$$

Next, going from stage $B\to C$, we are allowing this heated gas to expand isothermally. This is practically done by putting it in contact with a big heat sink. By expanding, we are able to capture that work ($W_{by}>0$) and use it. Since this is isothermal, we know that the internel energy is constant, and thus

$$Q=\int\mathrm{d}U+\int p\,\mathrm{d}V=W_{by}$$

Finally, we note that

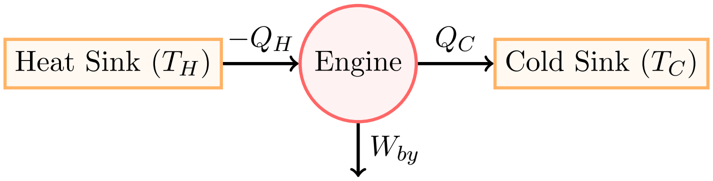
$$\Delta S_{sys}=\frac{Q}{T}=\frac{W_{by}}{T}>0$$

And that since the same heat is removed from the gas,

$$\Delta S_{\text{TOT}}=\frac{Q_{sys}}{T}+\frac{Q_{env}}{T}=0$$

since the net heat transfer is 0.

Finally, steps $C\to D$ and $D\to A$, are simply running $A\to B$ and $B\to C$ in reverse. The net change in entropy is 0 (since it is a cycle), but we get positive work from it.



We define the efficiency of an engine as

Definition 6 (Efficiency)**.**

$$\epsilon \equiv \frac{W_{by}}{Q_H}$$

the ratio of the usable work that we get from the heat sink.
Deriving the ideal efficiency is simple. Since $\Delta S \geq 0$,

$$0 \leq \Delta S = \frac{-Q_H}{T_H} + \frac{Q_C}{T_C}$$

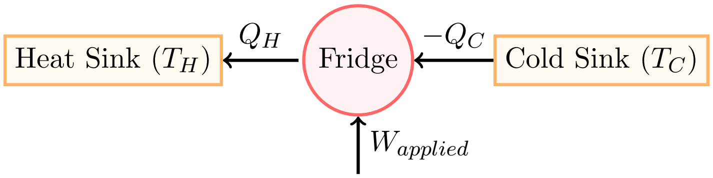
Equation 5.

$$\frac{Q_C}{Q_H} \geq \frac{T_C}{T_H}$$

Finally, with conservation of energy,

$$\begin{aligned}\epsilon &= \frac{W_{by}}{Q_H} = \frac{Q_H - Q_C}{Q_H} \\ &= 1 - \frac{Q_C}{Q_H} \leq 1 - \frac{T_H}{T_C}\end{aligned}$$

We may also run this in reverse, making a fridge (heat pump).



Engineers define the COP (coefficient of performance) as $1/\epsilon$, so that

$$\text{COP} = \frac{Q_C}{W_{applied}} \leq \frac{T_C}{T_H - T_C}$$

Isobaric processes and isochoric processes will be analyzed similarly to the isothermal and adiabatic above.

4 Boltzmann Factors

Jumping ahead to statistical mechanics, we talk about how we may derive certain quantities without equipartition applying. In particular, we may model the (relative) probability of a given macrostate following the Botlzmann distribution

Theorem 5 (Boltzmann Factors)**.**

$$p \propto \mathbf{exp}\left\{-\frac{E}{kT}\right\}$$

For example, consider the proportion of N_2 and O_2 gasses in the atmosphere. At heights h_1 and h_2, we find that

$$\begin{aligned}\frac{\mathbf{Pr}(N_2, h_2)}{\mathbf{Pr}(O_2, h_2)} &= \frac{\mathbf{Pr}(N_2, h_2)}{\mathbf{Pr}(N_2, h_1)}\frac{\mathbf{Pr}(N_2, h_1)}{\mathbf{Pr}(O_2, h_1)}\frac{\mathbf{Pr}(O_2, h_1)}{\mathbf{Pr}(O_2, h_1)} \\ &= \mathbf{exp}\left\{\frac{-(m_{N_2} - m_{O_2})g(h_2 - h_1)}{k_B T}\right\}\frac{\mathbf{Pr}(N_2, h_1)}{\mathbf{Pr}(O_2, h_1)}\end{aligned}$$

So that as the height/mass difference becomes more pronounced, we get stronger segregation. The primary application of this statistical modeling, with respect to this course, is that of semiconductors. Modeling these as two energy states E_V, E_C (valence and conduction), along with an intermediary metal, we can think of conduction as the flowing of electrons between these bands. Then, assuming that the flow of electrons into the valence band is the same as into the conduction band, we show that

Theorem 6 (Neutral Limit of Semiconductors)**.** *Let* $\Delta = E_V - E_C$*. Then,*

$$\rho \propto \mathbf{exp}\left\{\frac{-\Delta}{2k_B T}\right\}$$

Proof. First, we renormalize the energies as $E_C - \mu$, 0, and $E_V - \mu$ respectively, where μ is the potential of the intermediary metal. Now,

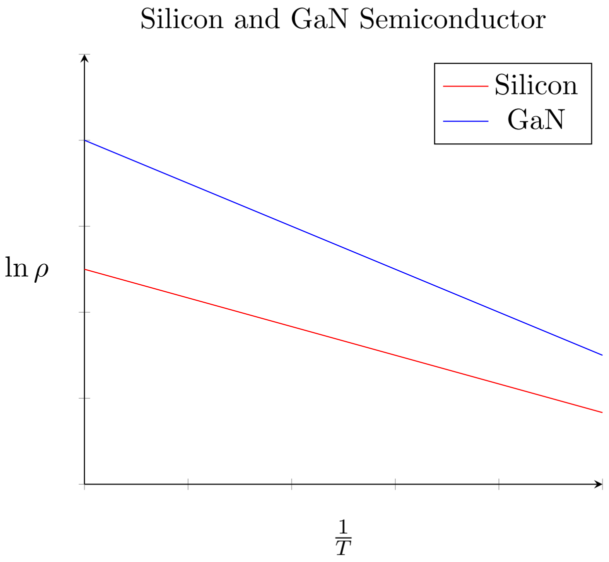
$$\begin{aligned}n_e &= \mathbf{Pr}(E_M \to E_C) \propto \mathbf{exp}\left\{\frac{-(E_C - \mu)}{k_B T}\right\} = \\ n_h &= \mathbf{Pr}(E_V \to E_M) \propto \mathbf{exp}\left\{\frac{-(\mu - E_V)}{k_B T}\right\}\end{aligned}$$

Finally, since the resistivity ρ is approximately the inverse of this probability,

$$\begin{aligned}\rho \propto \frac{1}{n_e} &= (n_e n_h)^{-\frac{1}{2}} \\ &= \mathbf{exp}\left\{\frac{-\Delta}{2k_B T}\right\}\end{aligned}$$

□

It is often useful to linearize these plots with $\ln \rho$ by $\frac{1}{T}$, to create so called *Arrhenius Plots*.



That is, since Gallium Nitride has a higher band gap, it has a steeper slope.
Finally, as consequence of the Boltzmann factors, we can study what happens when equipartition doesn't apply, in the extreme temperatures. A more detailed analysis is done in the course, modeling harmonic oscillators.

- When $T \to \infty$. every microstate becomes weighted equally, and therefore in a system with a finite k number of microstates (quantum), $S \to k_B \ln k$.
- When $T \to 0$, only the microstate with the lowest energy is possible, so $S \to k_B \ln 1 = 0$.

5 Free Energy

Finally, we conclude this course with a treatment of free energy and solutions. That is, we will focus heavily on deriving equilibrium states of matter, explaining the phase plots of water and other materials.
In these cases, we are assuming a fixed pressure and temperature of the system and environment. Thus, as we have a constant total volume and particles, we can characterize both sys/env with just the system macrovariables.
In equilibrium, we know that total entropy is maximized. That is,

$$\begin{aligned} 0 = \mathrm{d}S_{\text{TOT}} &= \mathrm{d}S_{\text{SYS}} + \mathrm{d}S_{\text{ENV}} \\ &= \mathrm{d}S_{\text{SYS}} + \left(\frac{1}{T}\,\mathrm{d}U_{\text{ENV}} + \frac{p}{T}\,\mathrm{d}V_{\text{ENV}}\right) \\ &= \mathrm{d}S_{\text{SYS}} - \frac{1}{T}\,\mathrm{d}U_{\text{SYS}} - \frac{p}{T}\,\mathrm{d}V_{\text{SYS}} \end{aligned}$$

and then, multiplying $-T$, we find that

Equation 6.

$$\mathrm{d}U - T\,\mathrm{d}S + p\,\mathrm{d}V = 0$$

Definition 7 (Gibbs)**.**

$$\mathrm{d}G = \mathrm{d}U - T\,\mathrm{d}S + p\,\mathrm{d}V$$

Definition 8 (Chemical Potential)**.**

$$\mathrm{d}G = \mu\,\mathrm{d}N$$

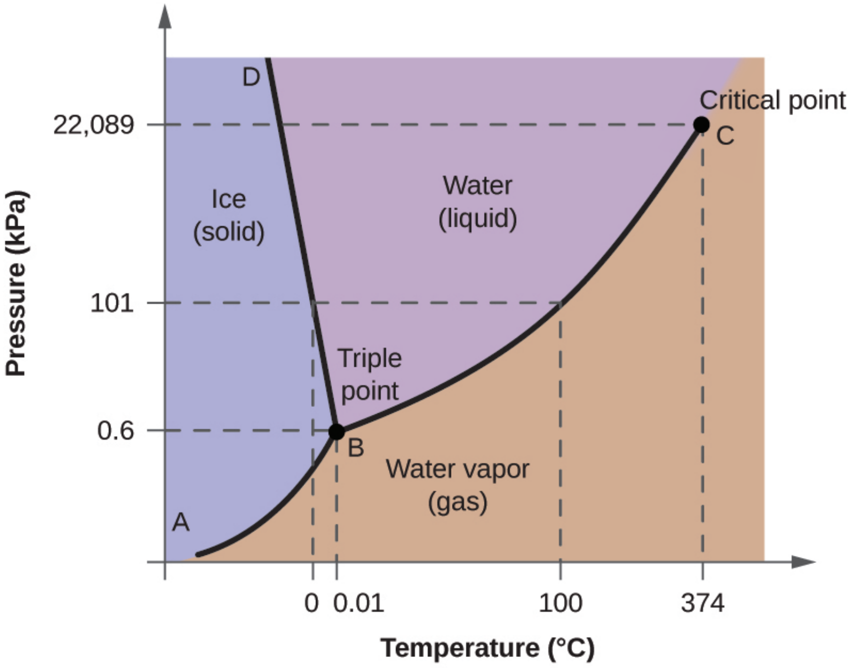
so that the equilibrium state is the minimum Gibbs free energy.
As an example of its use, we can re-derive the ideal gas law relation. That is, since

$$S = Nk_B \ln V + Ng(U)$$

we then find that

$$\begin{aligned} 0 = \frac{\mathrm{d}G}{\mathrm{d}V} &= \frac{\mathrm{d}U}{\mathrm{d}V} - T\frac{\mathrm{d}S}{\mathrm{d}V} + p\frac{\mathrm{d}V}{\mathrm{d}V} \\ &= 0 - \frac{TNk_B}{V} + p \end{aligned}$$

and thus, $pV = Nk_BT$.



A major use of this is in determining equilibrium phases [1]. We can examine the following diagram of water phase charts.

Since we are minimizing $G = U - TS + pV$, at low temperatures we tend to be minimizing U. Therefore, since the internel energy of solids is the least, followed by liquid then gas, we expect increasing the temperature to transition from ice to water to steam, which is true.

Further, along the phase line is when $\mathrm{d}G = 0$, since we are in equilibrium. In this case,

$$\frac{V}{N}\,\mathrm{d}p = \frac{S}{N}\,\mathrm{d}T$$

or equivalently, leting $\rho = \frac{N}{V}$ be the density,

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{S}{N}\rho$$

Starting at the line between ice and water, we notice that when we decrease temperature, we also decrease pressure. Transitioning from water to ice, we go along negative $\frac{\mathrm{d}p}{\mathrm{d}T}$, so thus $\Delta\rho < 0$. In other words, this freezing process is expanding.

Since most molecules compress when they freeze, they would have a positive slope between the solid-liquid barrier. This is just another case where water is special.

References

[1] Lumen Learning. Phase diagarms, 2010.

[2] James P. Wolfe. *Elements of Thermal Physics*. Hayden-McNeil Publishing, 2010.