Math 254A Lecture 15 Notes

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1 Models With Additional Thermodynamical Parameters

1.1 Recap

Suppose we have two thermodynamical systems with energy functions $\Phi_n : M_n \to [0, \infty)$ and $\widetilde{\Phi}_n : \widetilde{M}_n \to [0.\infty)$. Then

$$\lambda_n \left(\left\{ \frac{1}{n} \Phi_n \in I \right\} \right) = \exp \left(n \cdot \sup_{x \in I} s(x) + o(n) \right),$$

$$\widetilde{\lambda}_n \left(\left\{ \frac{1}{n} \Phi_n \in I \right\} \right) = \exp \left(n \cdot \sup_{x \in I} s(x) + o(n) \right).$$

We are studying what happens when we put the systems in thermal constant to constrain them so that the total energy is $\approx nE$. In equilibrium, energy split between the systems is decided by maximizing $s(x) + \widetilde{s}(E - x)$. If the exponent functions $s, \widetilde{s}$ are differentiable, then the condition is

$$s'(x) = \widetilde{s}'(E - x).$$

Hence, we denote $\frac{1}{s'(x)}$ as the **thermodynamic temperature** of the first system at energy x. In physics, the dependence of s on energy per particle x and any other parameters in the model is known as the **fundamental relation** of the system.[1]

1.2 Fundamental relation and equivalence of ensembles

In a laboratory, suppose we constrain the temperature of a system to be $T = 1/\beta$ (instead of controlling the total energy). Now we can look for energy per particle as a the root of the equation $s'(x) = \beta$ if you know the fundamental relation of the system.[2]

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[1] In practice, it may be easier to describe s^* instead.

[2] You can run into trouble here if s has any flat regions.

Alternatively, if we are also expecting equivalence of ensembles, we can make predictions about other thermodynamical quantities based directly on the canonical ensemble/the Gibbs measure

$$d\mu_{n,\beta}(p) = \frac{e^{-\beta\Phi_n(p)}\, d\lambda_n(p)}{Z_n(\beta)}.$$

Note that the microcanonical ensemble is determined by the total energy you're constraining around, while the canonical ensemble is determined by the temperature. So in this case, we can determine the behavior of the system using temperature, which is the quantity we can actually control in a lab.

1.3   Gas in a piston chamber

Example 1.1. Suppose we have gas in a chamber, where at one end, there is a piston. Assume the piston is frictionless.
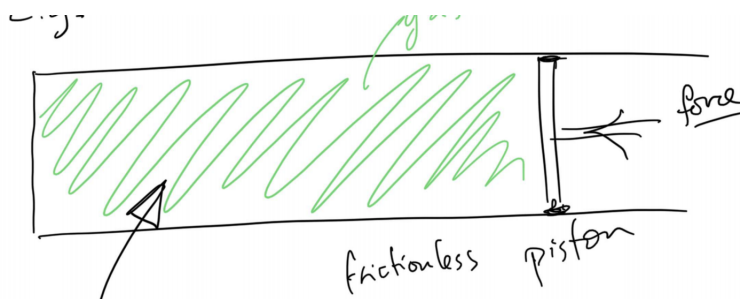
If the piston can slide back and forth, then it will be not moving when the gas inside is at the same pressure as the atmospheric pressure of the air outside the box. Thus, our system has an additional parameter, which can be modeled using the force on the piston, the pressure of the gas, or the total volume v of the chamber.

We'll begin our discussion with this example as the model, and then we will abstract out what we need to discuss general models with additional parameters. For simplicity, we will assume the area of the piston equals 1. How can we understand the dependence between the pressure and the volume from the fundamental relation?

Let's consider n "non-interacting" classical particles. The total energy of a particle with position r and momentum p is

$$\varphi(r,p) = \varphi_{\text{pot}}(r) + \frac{1}{2}|p|^2,$$

and the total energy of the system is

$$\Phi_n(r_1,\ldots,r_n,p_1,\ldots,p_n) = \sum_{i=1}^{n}\varphi(r_i,p_i).$$

We will now include the volume v as a parameter in all these functions. Assuming the particles bounce off the walls elastically,[3] we want to relate the pressure of the gas to the volume of the chamber. Forces are obtained as *gradients* of total potential energy, so the force on the piston is

$$\frac{\partial}{\partial v}\Phi_n(v, r_1, \ldots, r_n, p_1, \ldots, p_n) = \sum_{i=1}^{n} \frac{\partial \varphi_{\text{pot}}(v, r_i)}{\partial v}.$$

For most states $(r_1, \ldots, r_n, p_1, \ldots, p_n)$, this will be accurately predicted by

$$\left\langle \sum_{i=1}^{n} \frac{\partial \varphi_{\text{pot}}}{\partial v}(v, \cdot), \mu_{n,I} \right\rangle,$$

where $\mu_{n,I}$ is the microcanonical ensemble. Or, if we have equivalence of enesmbles, this is predicted by

$$\left\langle \sum_{i=1}^{n} \frac{\partial \varphi}{\partial v}(v, \cdot), \mu_{n,\beta} \right\rangle,$$

where $\mu_{n,\beta}$ is the canonical ensemble.

To understand this, look at

$$\begin{aligned}
\frac{\partial}{\partial v} s^*(v, \beta) &= \frac{\partial}{\partial v}\left\{ \frac{1}{n}\log \int e^{-\beta\Phi_n(v,\cdot)}\, d\lambda_n \right\} \\
&= \frac{1}{n}\frac{\int -\beta \frac{\partial\Phi_n}{\partial v} e^{-\beta\Phi_n}\, d\lambda_n}{\int e^{-\beta\Phi_n}\, d\lambda_n} \\
&= -\frac{1}{n}\beta \left\langle \frac{\partial\Phi_n}{\partial v}, \mu_{n,\beta} \right\rangle.
\end{aligned}$$

So

$$\frac{\partial}{\partial v}F(v, \beta) = \left\langle \frac{\partial\Phi_n}{\partial v}, \mu_{n,\beta} \right\rangle,$$

where

$$F(v, \beta) = -\frac{n}{\beta}s^*(v, \beta) = Tns^*(v, \beta).$$

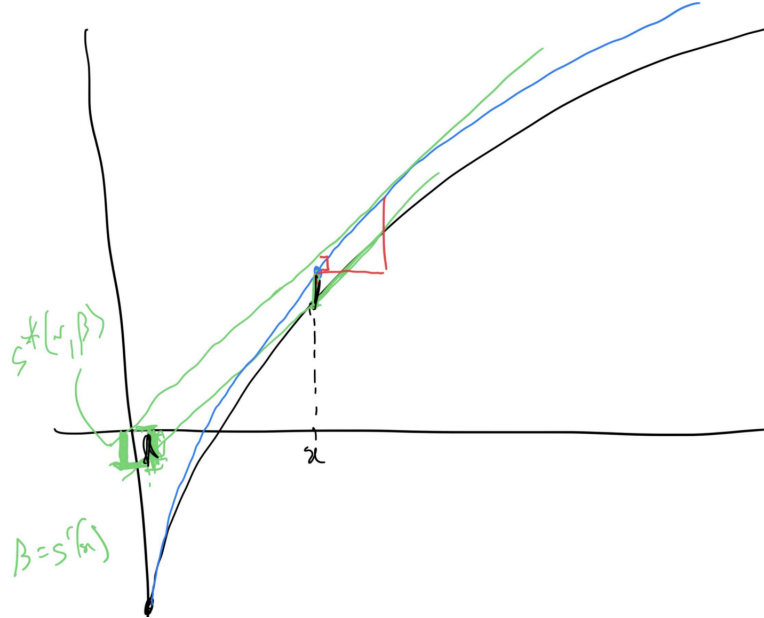This is known as the **free energy**, the **Helmholtz function**, or the **Helmholtz free energy**. So the pressure is

$$P = \frac{\partial}{\partial v}F(v, \beta) = \frac{\partial}{\partial v}[-T\log Z_n(v, \beta)].$$

Here is another way to get this in terms of s itself:

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[3]

Lemma 1.1. *If $s(v,x)$ is strictly concave in β and C^2 in both parameters, then*

$$\frac{\partial}{\partial v}s^*(v,\beta) = \frac{\partial}{\partial x}s(v,x).$$

Proof. Here is a proof by picture. Draw $s(,x)$ and $s(v+dv,x)$:

Recall that $s^*(v,\beta)$ is the vertical-axis intercept when we draw the tangent line to s at x. Here, $\beta = s'(x)$. On the tangent line to the new blue curve in this picture, the slope maybe changed a little bit. Instead, find a place where a tangent of the same slope hits the blue curve and consider the difference of those intercepts. The difference between these changes in the intercept end up being a second order difference, so they disappear in the derivative. $\qquad\square$

Once we know s, this leads to equations that relate V, P, T or V, P, E, etc. Once you have any two parameters, you can solve for the third. Any such equation is called an **equation of state**.