Math 254A Lecture 16 Notes

Daniel Raban

May 3, 2021

1 The Ideal Gas Law and Discretization

1.1 Recap

Last time, we set up a model with total energy $\Phi_n : I \times M_n \to [0, \infty)$, where I is an set specifying an extra parameter, such as the volume v of the enclosing system. Let $S_n(V, x) := \log \lambda_n(\{\frac{1}{n}\Phi_n(v, \cdot) \approx x\})$, and we assume that $\frac{1}{n}S_n(v, x) \to s(v, x)$, where s is concave in x, etc. We have the partition function $Z_n(v, \beta) = \int e^{-\beta \Phi_n} \, d\lambda_n$, and we assume that $\frac{1}{n} \log Z_n(v, \beta) \to s^*(v, \beta)$, where $\beta > 0$. These are related by using the Fenchel-Legendre transform:

$$s(v, x) = \inf_{\beta > 0} \{s^*(v, \beta) + \beta x\},$$

where the inf is achieved at $\beta = \frac{\partial}{\partial x} s(v, x)$.

In our piston chamber example, the "pressure" P associated to v was

$$\left\langle \frac{\partial \Phi_n(v, \cdot)}{\partial v}, \mu_{n,\beta} \right\rangle = \frac{\partial}{\partial v} \underbrace{[-T \log Z_n(v, \beta)]}_{=F(v,\beta)},$$

where $F(v, \beta)$ is the **Helmholtz free energy** and $T := 1/\beta$ is the **thermodynamic temperature**.
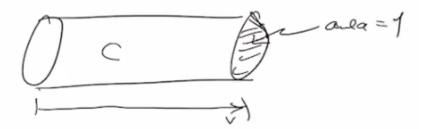
$$\approx \frac{\partial}{\partial v}[-Tns^*(v, \beta)]$$

Here are the assumptions we have been making here:

- For most microscopic states, this quantity stays close to its average with respect to to the microcanonical ensemble.

- We can replace the microcanonical ensemble by the canonical ensemble.

- We are assuming that we can interchange integration and differentiation in the above calculation (this is fortunately not hard to justify using convexity arguments).

1.2   The ideal gas law

Assume a gas of n (mass 1) non-interacting particles is in a region (cylinder C with cross-sectional area 1 and length v).

The state is $(r_1, \ldots, r_n, p_1, \ldots, p_n) \in (\mathbb{R}^3 \times \mathbb{R}^3)^n$, and the potential energy is

$$\varphi_{\text{pot}}(r) = \begin{cases} 0 & r \in C \\ \infty r \notin C. \end{cases}$$

The total energy is

$$\Phi_n(r_1, \ldots, r_n, p_1, \ldots, p_n) = \begin{cases} \sum_{i=1}^n \frac{1}{2}|p_i|^2 & r_i \in C \; \forall i \\ \infty & \text{otherwise.} \end{cases}$$

Our goal is to understand the pressure in terms of temperature and volume. We understand this through

$$Z_n(v, \beta) = \int \cdots \int e^{-\beta \Phi_n} \, dm_3^{\times n}(r_1, , \ldots, r_n) \, dm_3^{\times n}(p_1, \ldots, p_n)$$

$$= \int_{C^n} dr_1 \cdots dr_n \cdot \int \cdots \int e^{-\beta \sum_{i=1}^n |p_i|^2/2} \, dp_1 \cdots dp_n$$

$$= v^n \cdot \left(\int e^{-\beta |p|^2/2} \, dp \right)^n$$

$$= v^n \cdot \left(\left(\frac{2\pi}{\beta} \right)^{3/2} \right)^n.$$

Then

$$F_n = T \log Z_n = T n \log V - \frac{3Tn}{2} \log(2\pi T),$$

and so the pressure is

$$P = \frac{\partial F_n}{\partial v} = \frac{Tn}{v}.$$

Thus, we get the **Ideal Gas Law**:[1]

$$PV = nT.$$

In Gay-Lussac's version of this law, he derived a slightly more complicated-looking expression

$$PV = \text{const} \cdot n \cdot (\text{const} + \theta),$$

where θ is the celsius temperature and the constant next to it is $\approx 273.16°$ C.

1.3 Discretization in models with interaction

Suppose we have n particles in a region $R_n \subseteq \mathbb{R}^3$ with volume $|R_n|$. Then the position is $(r_1, \ldots, r_n) \in R_n^n$, and

$$\Phi_n(r_1, \ldots, r_n) = \sum_{i=1}^{n} \varphi_{\text{pot}}(r_i) + \sum_{i \neq j} \varphi_{\text{int}}(r_i - r_j) + \sum_{i=1}^{n} \frac{1}{2}|p_i|^2.$$

Here, the measure is $\lambda_n = m_3^{\times n} \times m_3^{\times n}$. The entropy

$$s_n(x) = \log \lambda_n(\{(r_1, \ldots, r_n, p_1, \ldots, p_n) : \tfrac{1}{n}\Phi_n \approx x\}).$$

We have a new kind of limit: The region should depend on n, so that $\frac{|R_n|}{n} \to$ some limit $= v$. This little v is called the **molar volume**.

Note that

$$\lambda_n(\{(r_1, \ldots, r_n) \in R_n^n\}) = |R_n|^n \sim (nv)^n = n^n v^n.$$

This blows up with n. The solution is to not care about the ordering of the positions of the particles (treating the particles as indistinguishable). Thus, we actually define $\lambda_n = \frac{1}{n!} m_3^{\times n} \times m_3^{\times n}$, and this quantity $\sim (v/e)^n$.

With this choice of λ_n now look at

$$Z_n(\beta) = \int_{R_n^n} e^{-\beta \sum \varphi_{\text{pot}}(r_i) - \beta \sum \varphi_{\text{int}}(r_i - r_j)} \, dr_1 \cdots dr_n \cdot \int_{(\mathbb{R}^3)^n} e^{-(\beta/2)(|p_1|^2 + \cdots + |p_n|^2)} \, dp_1 \cdots dp_n$$

$$= \frac{1}{n!} \int_{R_n^n} e^{-\text{potential terms}} \, dr_1 \cdots dr_n \cdot \left(\frac{2\pi}{\beta}\right)^{3n/2}.$$

So we get

$$\log Z_n(\beta) = \log \left(\frac{1}{n!} \int_{R_n^n} (\cdots) \, dr_1 \cdots dr_n\right) + \frac{3n}{2} \log \frac{2\pi}{\beta}.$$

---

[1] If you are using standard physical units, you need a constant in here to facilitate the conversion of units.

To "discretize" such a model, focus on the first term, ignore the second term, and then discretize $R_n^n \subseteq (\mathbb{R}^3)^n$ to $(R_n \cap \varepsilon\mathbb{Z}^3)^n \subseteq (\varepsilon\mathbb{Z}^3)^n$. Then we replace m_3 with counting measure times ε^3.

Next time, we will show how these considerations can allow us to derive the ideal gas law again.