

# Math 254A Lecture 16 Notes

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## 1 The Ideal Gas Law and Discretization

### 1.1 Recap

Last time, we set up a model with total energy  $\Phi_n : I \times M_n \rightarrow [0, \infty)$ , 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  $\frac{1}{n}S_n(v, x) \rightarrow s(v, x)$ , 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  $\frac{1}{n} \log Z_n(v, \beta) \rightarrow s^*(v, \beta)$ , 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 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  $(r_1, \dots, r_n, p_1, \dots, p_n) \in (\mathbb{R}^3 \times \mathbb{R}^3)^n$ , 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

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

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

$$\begin{aligned} Z_n(v, \beta) &= \int \dots \int e^{-\beta \Phi_n} dm_3^{\times n}(r_1, \dots, r_n) dm_3^{\times n}(p_1, \dots, p_n) \\ &= \int_{C^n} dr_1 \dots dr_n \cdot \int \dots \int e^{-\beta \sum_{i=1}^n |p_i|^2 / 2} dp_1 \dots dp_n \\ &= v^n \cdot \left( \int e^{-\beta |p|^2 / 2} dp \right)^n \\ &= v^n \cdot \left( \left( \frac{2\pi}{\beta} \right)^{3/2} \right)^n. \end{aligned}$$

Then

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

and so the pressure is

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

Thus, we get the **Ideal Gas Law**:<sup>1</sup>

$$PV = nT.$$

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  $\theta$  is the Celsius temperature and the constant next to it is  $\approx 273.16^\circ \text{C}$ .

### 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  $(r_1, \dots, r_n) \in R_n^n$ , and

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

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

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

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

Note that

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

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  $\lambda_n$  now look at

$$\begin{aligned} Z_n(\beta) &= \int_{R_n^n} e^{-\beta \sum \varphi_{\text{pot}}(r_i) - \beta \sum \varphi_{\text{int}}(r_i - r_j)} dr_1 \dots dr_n \cdot \int_{(\mathbb{R}^3)^n} e^{-(\beta/2)(|p_1|^2 + \dots + |p_n|^2)} dp_1 \dots dp_n \\ &= \frac{1}{n!} \int_{R_n^n} e^{-\text{potential terms}} dr_1 \dots dr_n \cdot \left(\frac{2\pi}{\beta}\right)^{3n/2}. \end{aligned}$$

So we get

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

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<sup>1</sup>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  $\varepsilon^3$ .

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