Math 254A Lecture 17 Notes

Daniel Raban

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1 Deriving The Ideal Gas Law With Nonconstant Volume

1.1 Recap

Last time, we had a model of n interacting particles in a region $R_n \subseteq \mathbb{R}^3$. We will keep the volume per particle constant:

$$\frac{|R_n|}{n} \to v.$$

Then the phase space is $M_n = R_n \times \mathbb{R}^3$ for positions and momenta, and the measure is $\lambda_n = \frac{1}{n!} m_3 \times m_3$, where the $\frac{1}{n!}$ shows that we are treating the particles as indistinguishable. The total energy of our particles is

$$\Phi_n(r_1, \ldots, r_n, p_1, \ldots, p_n) = \sum_{i=1}^n \varphi_{\text{pot}}(r_i) + \sum_{i,j} \varphi_{\text{int}}(r_i - r_j) + \sum_{i=1}^n \frac{1}{2} |p_i|^2,$$

so we have potential energy, interaction energy, and kinetic energy terms. The partition function is

$$Z_n(\beta) = \int e^{-\beta \Phi_n} \, d\lambda_n = \underbrace{\widetilde{Z}_n(\beta)}_{\text{pot. + int. energy part}} \cdot \underbrace{\left(\frac{2\pi}{\beta} \right)^{3n/2}}_{\text{kinetic energy part}},$$

where

$$\widetilde{Z}_n(\beta) = \frac{1}{n!} \int \cdots \int_{R_n^n} e^{-\beta \sum_{i=1}^n \varphi_{\text{pot}}(r_i) - \beta \sum_{i,j} \varphi_{\text{int}}(r_i - r_j)} \, dm_3^{\times n}.$$

1.2 Derivation of the ideal gas law with nonconstant volume

Now discretize[1] space: pick $\varepsilon > 0$ and let $B_n = R_n \cap \varepsilon \mathbb{Z}^3$. We will analyze the resulting approximation to $\widetilde{Z}_n(\beta)$ and then let $\varepsilon \downarrow 0$ to derive an equation of state. The approximation

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[1]Discretization is not actually necessary, but without it, our arguments will take too long for the purposes of this course.

to $\widetilde{Z}_n(\beta)$ is to

$$\text{replace } \int \cdots \int_{R_n^n} \text{ with } \frac{1}{n!} \sum_{\substack{r_1,\ldots,r_n \in B_n \\ r_1,\ldots,r_n \text{ distinct}}} .$$

or equivalently with the sum

$$\sum_{\omega \subseteq B_n, |\omega|=n} .$$

We will actually use the indexing

$$\sum_{\substack{\omega \in \{0,1\}^{B_n}, \\ |\omega|=n}} , \qquad \text{where } |\omega| = \sum_{x \in B_n} \omega_i.$$

So we need to analyze

$$\widehat{Z}_n(\beta) = \sum_{\substack{\omega \in \{0,1\}^{B_n} \\ |\omega|=n}} e^{-\beta \sum_{i \in B_n} \varphi_{\text{pot}}(i) \cdot \omega(i)} e^{-\beta \sum_{i,j \in B_n} \varphi_{\text{int}}(i-j)\omega_i\omega_j}.$$

Now let's rederive the ideal gas law again: $\varphi_{\text{pot}} = \varphi_{\text{int}} = 0$, leaving

$$\widehat{Z}_n(\beta) = |\{\omega \in \{0,1\}^{B_n} : |\omega| = n\}| = \binom{|B_n|}{n}$$

$$= \binom{|B_n|}{\frac{n}{|B_n|}|B_n|}$$

where $n/|B_n| \to \varepsilon^3/v$.

$$= \exp\left(|B_n| \cdot H\left(\frac{\varepsilon^3}{v}, 1 - \frac{\varepsilon^3}{v}\right) + o(|B_n|)\right)$$

As $n \to \infty$, this looks like

$$= \exp\left(n\frac{v}{\varepsilon^3} H\left(\frac{\varepsilon^3}{v}, 1 - \frac{\varepsilon^3}{v}\right) + o(n)\right).$$

So $\frac{1}{n}\log\widehat{Z}_n(\beta) \to \frac{v}{\varepsilon^3}H(\frac{\varepsilon^3}{v}, 1 - \frac{\varepsilon^3}{v})$ as $n \to \infty$. So in this model.

$$P = \frac{\partial}{\partial}[-T\log\widehat{Z}_n(\beta)]$$

$$= nT\frac{\partial}{\partial v}\left[\frac{v}{\varepsilon^3}H\left(\frac{\varepsilon^3}{v}, 1 - \frac{\varepsilon^3}{v}\right)\right] + o(n)$$

Now we calculate

$$\frac{\partial}{\partial v}\left[\frac{v}{\varepsilon^3}\left(-\frac{\varepsilon^3}{v}\log\frac{\varepsilon^3}{v} - \left(1 - \frac{\varepsilon^3}{v}\right)\log\left(1 - \frac{\varepsilon^3}{v}\right)\right)\right]$$

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$$= \frac{\partial}{\partial v} \left[\log \frac{v}{\varepsilon^3} - \left(\frac{v}{\varepsilon^3} - 1 \right) \log \left(1 - \frac{\varepsilon^3}{v} \right) \right]$$

$$= \frac{1}{v} - \frac{\partial}{\partial v} \left[\left(\frac{v}{\varepsilon^3} - 1 \right) \log \left(1 - \frac{\varepsilon^3}{v} \right) \right],$$

where the right term becomes negligible as $\varepsilon \to 0$ (there may be some calculation errors).

So

$$P = \frac{nT}{v} + o_{\varepsilon \downarrow 0}(n),$$

and we get the ideal gas equation of state, $PV = nT$, after letting $\varepsilon \to 0$. The value of this method is that we can vary the volume as we increase the number of particles. If we increased the number of particles without increasing the volume, the pairwise interactions of the particles may blow up. Note that most quantities here admit direct control or observation in the laboratory.

Here is how we may plot experimental data following the ideal gas law. The lines are isotherms, curves where T is held constant.


1.3 The van der Waals equation of state

In 1872, van der Waals wrote the more accurate following equation of state

$$\underbrace{\left(P + \frac{a}{v^2} \right)}_{\substack{\text{effective} \\ \text{pressure}}} \cdot \underbrace{(v - b)}_{\substack{\text{effective} \\ \text{compressible} \\ \text{volume}}} = nT,$$

where a, b are constants. This equation tells you what the effective addition to pressure a/v^2 is when the volume changes, accounting for the approximation errors in our model.

This equation of state predicts real world behavior in a larger range of contexts than the ideal gas law. Here is a picture of what this equation of state predicts:
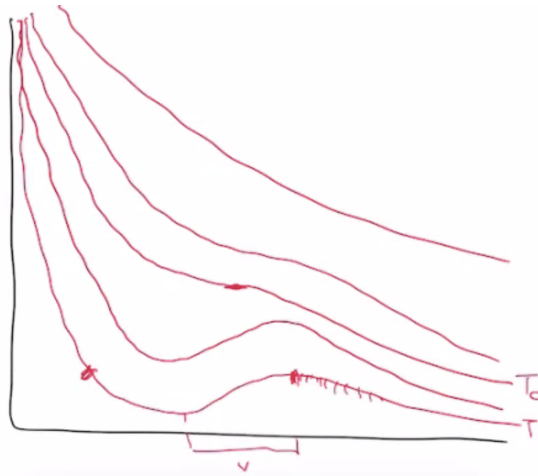
However, this predicts that at low temperatures, gasses can "catastrophically collapse." Maxwell later adjusted the model by assuming that we adjust the curve so the total area under the curve is the total work. This is known as "Maxwell's equal area correction." We will discuss this story next time.