Math 254A Lecture 18 Notes

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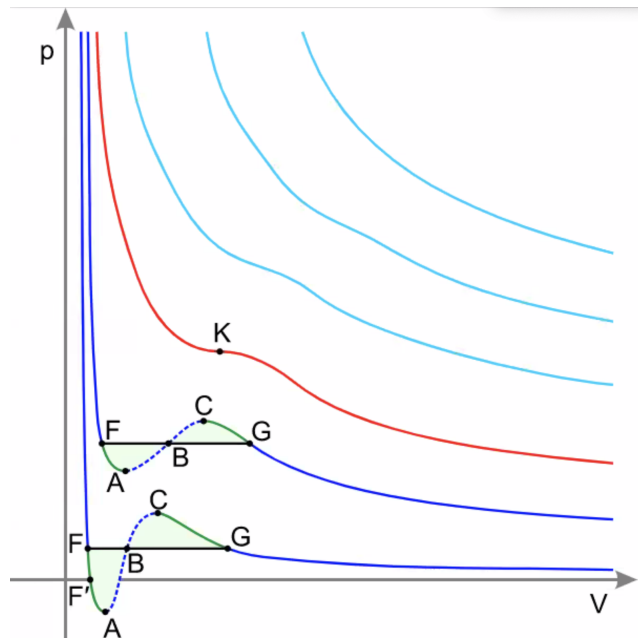# 1 Deriving van der Waal's Equation

1.1 Recap

Last time, we derived the ideal gas law

$$Pv = nT,$$

where the volume is not held constant as the number n of particles increase. We mentioned van der Waal's equation, which is a better description of real gasses:

$$\left(P + \frac{a}{v^2}\right)(V - b) = nT,$$

where a and b are constants. Here is what the equation predicts:

The flat regions in this picture are the Maxwell correction to van der Waal's equation. Our next goal is to derive this equation from some simple model.

1.2   Overview of van der Waal's equation

The continuous model (with the kinetic part removed) has the partition function

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

The discrete analogue is

$$\widetilde{Z}_n(\beta) = \sum_{\substack{\omega \in \{0,1\}^{B_n} \\ |\omega| = n}} \exp\left(-\beta \sum_{i \in B_n} \varphi(i)\omega_i - \beta \sum_{i,j \in B_n} \varphi_{\text{int}}(i-j)\omega_i\omega_j\right),$$
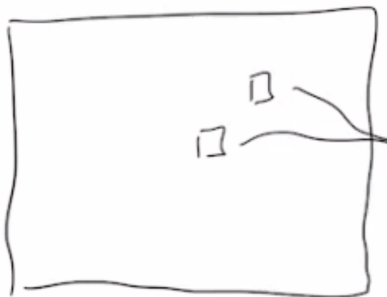
where $B_n = R_n \cap \varepsilon \mathbb{Z}^3$.

Under what conditions can we derive van der Waal's equation? We will do this for the case $b = 0$, i.e.

$$\left(P + \frac{a}{v^2}\right) v = nT.$$

(Getting the case $b > 0$ is similar but more intricate, so we will not do it for the sake of time.)

Imagine two tiny regions in a gas.

The mass in each tiny region is proportional to the density, $1/v$. So the force between the two regions is dependent on $1/v$. This gives intuition for why there should be a $1/v$ in the equation. This idea of interactions between molecules will lead to the equation.[1]

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[1] These forces between molecules are now known as **van der Waals forces**.

1.3 Setup and notation

To incorporate a limit of "long range forces," fix an attractive potential energy of interaction $\varphi : \mathbb{R}^3 \to [0, \infty)$ (since φ is attractive, to avoid having a negative potential, we assume φ is positive and just change the sign in the partition function equation). We will also assume

- $\varphi \in C^1$,

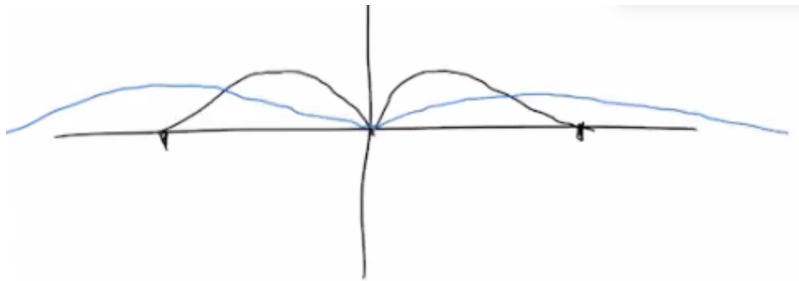- $\varphi(x) = 0$ for $|x| \geq 1$.

- $\varphi(x) = \varphi(-x)$.

Let
$$\varphi^r(x) = \frac{1}{r^3} \varphi\left(\frac{x}{r}\right), \qquad \text{for } r > 0,$$
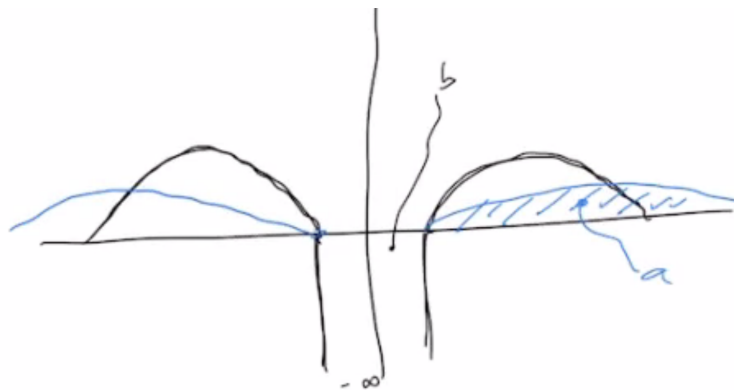so
$$\int \varphi^r \, dm_3 = \int \varphi \, dm_3 = a$$
for all $r > 0$. We will be taking $n \to \infty$ and then taking $r \to \infty$. Here's what this looks like:

To get $a > 0$ and $b > 0$, we would need to treat a picture like this:

We want to estimate
$$\widetilde{Z}_n(\beta) = \sum_{\substack{\omega \in \Omega_n \\ |\omega| = N_n}} \exp\left(-\beta \Phi_n^r(\omega)\right),$$
where $\Omega_n := \{0,1\}^{B_n}$, N_n is the number of particles in B_n, and $B_n = \{1,\ldots,n\}^3$ (note we are changing notation to make n be some geometric parameter rather than the number of particles). We also have
$$\Phi_n^r(\omega) = \sum_{i,j \in B_n} \varphi^r(\varepsilon(i-j))\omega_i\omega_j.$$

1.4 Splitting space into boxes with mass pooled around the centers

We want to estimate $\frac{1}{n} \log \widehat{Z}_n(\beta)$, and we will let $n, r \to \infty$, $\varepsilon \to 0$, and differentiate with respect to v. Here is a picture of how we will do it:
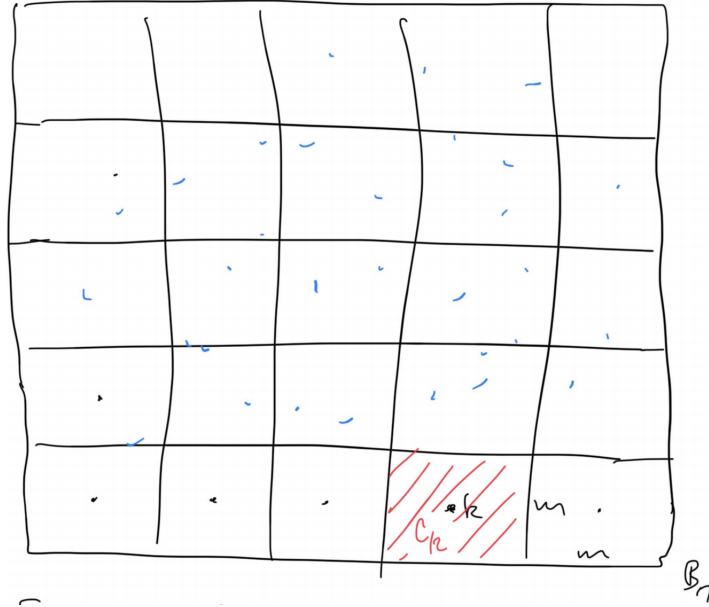
Fix another $m \in \mathbb{N}$, and divide B_n into $m \times m$ boxes. Let $\mathcal{C}_n$ be the set of centers of these boxes. If $k \in \mathcal{C}_n$, then C_k will be the box with center k. (We will assume that $m \mid n$ for simplicity.). Picture $1 \ll m \ll r$, and let $\omega \in \Omega_n$ with $|\omega| = N_n$. We will define a map $D : \Omega_n \to \widetilde{\Omega}_n = \{0, 1/m^3, 2/m^3, \ldots, 1\}^{\mathcal{C}_n}$ by

$$D(\omega)_k = \frac{1}{m^3} \sum_{i \in C_k} \omega_i.$$

The idea is that $\Phi_n^r(\omega)$ is approximately a function only of $D(\omega)$, provided $r \gg m$.

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Define the **effective energy** of a configuration $\rho \in \widetilde{\Omega}_n$:

$$\widetilde{\Phi}_n^r(\rho) = m^6 \sum_{k,\ell \in \mathcal{C}_n} \rho_k \rho_\ell \varphi^r(\varepsilon(k - \ell))$$

Lemma 1.1. *If $D(\omega) = \rho$, then*

$$\Phi_n^r(\omega) = \widetilde{\Phi}_n^r(\rho) + O\left(n \cdot \frac{1}{mr}\right).$$

Proof. Suppose $i \in C_k$ and $j \in C_\ell$. Then

$$\varphi^r(\varepsilon(i - j)) - \varphi^r(\varepsilon(k - \ell)) \le \|\nabla \varphi^r\|(|\varepsilon(i - k)| + |\varepsilon(j - \ell)|)$$
$$= \frac{1}{r^4}\|\nabla \varphi\| \cdot O\left(\frac{m\varepsilon}{r^4}\right)$$
$$= O\left(\frac{m\varepsilon}{r^4}\right).$$

Therefore,

$$\left| \sum_{i \in C_k, j \in C_\ell} \varphi^r(\varepsilon(i - j))\omega_i \omega_j - m^6 \varphi^r(\varepsilon(k - \ell))\rho_k \rho_\ell \right|$$
$$= \left| \sum_{i \in C_k, j \in C_\ell} [\varphi^r(\varepsilon(i - j)) - \varphi^r(\varepsilon(k - \ell))]\omega_i \omega_j \right|$$
$$\le m^6 O\left(\frac{m\varepsilon}{r^4}\right)$$
$$= O\left(\frac{m^7 \varepsilon}{r^4}\right).$$

All that remains will be to sum over all pairs of boxes, which we will do next time. $\quad\square$