Math 254A Lecture 21 Notes

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1 Deriving van der Waal's Equation: The Final Chapter

1.1 Combining accumulated approximations for the partition function

So far, we had our original partition function

$$Z_n^r = \frac{1}{N_n!}\int \cdots \int_{R_n^{N_n}} e^{-\beta \sum_{i,j} \varphi^r(q_i - q_j)} \, dm_3^{\times N_n}(q_1, \dots, q_{N_n}.$$

We replaced it with the discretized partition function

$$\widetilde{Z}_n^r = \sum_{\substack{\omega \in \{0,1\}^{B_n} \\ |\omega| = N_n}} e^{-\beta \Phi_n^r(\omega)}, \qquad B_n = R_n \cap \varepsilon \mathbb{Z}^3,$$

which is what we will prove results about. We also introduced the **effective partition function**

$$\widehat{Z}_n^r = \sum_{\substack{\rho \in \widetilde{\Omega}_n \\ |\rho| = N_n/m^3}} e^{n^3 W(\rho) - \beta \widetilde{\Phi}_n^r(\rho)},$$

which approximates $\widetilde{Z}_n^r$.

So far, our approximations have been:

- (Unproved heuristic):

$$Z_n^r \approx \widetilde{Z}_n^r e^{[\text{small}] \cdot n} \qquad \text{as } n \to \infty.$$

- $$\begin{aligned} \log \widetilde{Z}_n^r &= \log \widehat{Z}_n^r + O\left(\frac{n^3 m}{\varepsilon^2 r}\right) + o(n^3) \\ &= n^3 \max_\rho \left\{ W(p) - \frac{\beta}{n^3} \widetilde{\Phi}_n^r(\rho) \right\} + O\left(n^3 \cdot \frac{\log m}{m^3}\right) + O\left(\frac{n^3 m}{\varepsilon^2 r}\right) + o(n^3) \end{aligned}$$

$$= n^3 \left[F_{\beta\alpha(m,\varepsilon,r)} \left(\frac{\varepsilon^3}{v} \right) + \cancel{o_{n\to\infty}(1)} + \cancel{O\left(\frac{1}{m^3} \right)} \right] + O\left(n^3 \cdot \frac{\log m}{m^3} \right)$$
$$+ O\left(\frac{n^3 m}{\varepsilon^2 r} \right) + o(n^3)$$

Recall that $f_\gamma(x) = H(x, 1-x) + \gamma x^2$ and $F_\gamma(x)$ is the concave envelope of $f_\gamma(x)$ for $0 \le x \le 1$.

$$= n^3 \left[F_{\beta\alpha/\varepsilon^3} \left(\frac{\varepsilon^3}{v} \right) + \cancel{O\left(\frac{m}{\varepsilon^2 r} \right)} \right] + \text{(other error terms)}$$
$$= n^3 F_{\alpha\beta/\varepsilon^3} \left(\frac{\varepsilon^3}{v} \right) + O\left(n^3 \cdot \frac{\log m}{m^3} \right) + O\left(\frac{n^3 m}{\varepsilon^2 r} \right) + o(n^3).$$

We want everything in terms of N_n, rather than in terms of the volume of the box. So let's write

$$\begin{aligned} \frac{1}{N_n} \log \widehat{Z}_n^r &= \frac{1}{n^3} \frac{n^3}{N_n} [\text{above stuff}] \\ &= \left(\frac{v}{\varepsilon^3} + o_{n\to\infty}(1) \right) [\text{above stuff}] \\ &= \left(\frac{v}{\varepsilon^3} + o(1) \right) \left[F_{\alpha\beta/\varepsilon^3} \left(\frac{\varepsilon^3}{v} \right) + O\left(\frac{\log m}{m^3} \right) + O\left(\frac{m}{\varepsilon^2 r} \right) + o(1) \right]. \end{aligned}$$

1.2 Taking limits to find the asymptotic behavior of the partition function

Let $n \to \infty$. Then $r \to \infty$ and $m \to \infty$ (with $m = \sqrt{r}$). Then, we will let $\varepsilon \to 0$. We get

$$\lim_{r\to\infty} \lim_{n\to\infty} \frac{1}{N_n} \log \widetilde{Z}_n^r = \frac{v}{\varepsilon^3} F_{\alpha\beta/\varepsilon^3} \left(\frac{\varepsilon^3}{v} \right).$$

What happens here as $\varepsilon \to 0$?

We need the following lemma (proven in Homework 3):

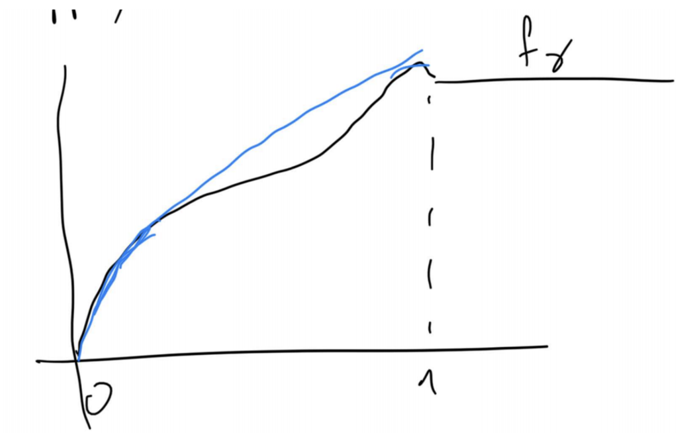
Lemma 1.1. *Suppose $f : [0,\infty) \to \mathbb{R}$ is continuous with concave envelope $F : [0,\infty) \to \mathbb{R}$. Assume $f(x)/x \to 0$ as $x \to \infty$. Then $g : [0,\infty) \to \mathbb{R}$, defined by*

$$g(v) = \begin{cases} v \cdot f(1/v) & v > 0 \\ 0 & v = 0, \end{cases}$$

has concave envelope equal to

$$\begin{cases} v \cdot F(1/v) & v > 0 \\ 0 & v = 0. \end{cases}$$

We will apply this to f_γ (making it flat to the right of the unit interval):



So the remaining expression above is the concave envelope of $\frac{v}{\varepsilon^3} f_{\alpha\beta/\varepsilon^3}(\frac{\varepsilon^3}{v})$, which is explicit. This is

$$
\begin{aligned}
&= \frac{v}{\varepsilon^3}\left[-\frac{\varepsilon^3}{v}\log\frac{\varepsilon^3}{v} - \left(1-\frac{\varepsilon^3}{v}\right)\log\left(1-\frac{\varepsilon^3}{v}\right) + \frac{\alpha\beta}{\varepsilon^3}\left(\frac{\varepsilon^3}{v}\right)^2\right] \\
&= \log\frac{v}{\varepsilon^3} - \left(\frac{v}{\varepsilon^3}-1\right)\log\left(1-\frac{\varepsilon^3}{v}\right) + \frac{\alpha\beta}{v} \\
&= \log v - \log\varepsilon^3 + \left(\frac{v}{\varepsilon^3}-1\right)\left(\frac{\varepsilon^3}{v} + O\left(\frac{\varepsilon^6}{v^2}\right)\right) + \frac{\alpha\beta}{v} \\
&= \log v - \log\varepsilon^3 + 1 + O\left(\frac{\varepsilon^3}{v}\right) + \frac{\alpha\beta}{v}.
\end{aligned}
$$

In our original formulas for $\widehat{Z}_n^r$ and $\widetilde{Z}_n^r$, we should have had a factor of $(\varepsilon^3)^{N_n}$ to account for the number of particles per box. Putting that in (and carrying it throughout the whole calculation), we are left with

$$
\frac{v}{\varepsilon^3} f_{\alpha\beta/\varepsilon^3}\left(\frac{\varepsilon^3}{v}\right) = \log v + 1 + \frac{\alpha\beta}{v} + O\left(\frac{\varepsilon^3}{v}\right).
$$

This is a uniform limit as $\varepsilon \downarrow 0$ for v bounded away from 0. Check that we also get convergence of the derivatives in v and that we get the same convergence for the concave envelopes. So

$$
\lim_{r\to\infty}\lim_{n\to\infty}\frac{1}{N_n}\log\widetilde{Z}_n^r = \text{conc. env. of } \underbrace{\left(\log v + 1 + \frac{\alpha\beta}{v}\right)}_{g(v)}.
$$

1.3 Recovering van der Waal's equation and Maxwell's equal area correction

What does this have to do for the van der Waal's equation? Maxwell's equal area correction is precisely what you get when you replace $\log v + 1 + \frac{\alpha\beta}{v}$ by its concave envelope. Explicitly, we get:

$$P = \frac{\partial}{\partial v}[T \log \text{partition function}].$$

We have

$$\frac{\partial}{\partial v}\left[\frac{1}{\beta}\log v + \frac{1}{\beta} + \frac{1}{v}\right] = \frac{1}{\beta v} - \frac{\alpha}{v^2},$$

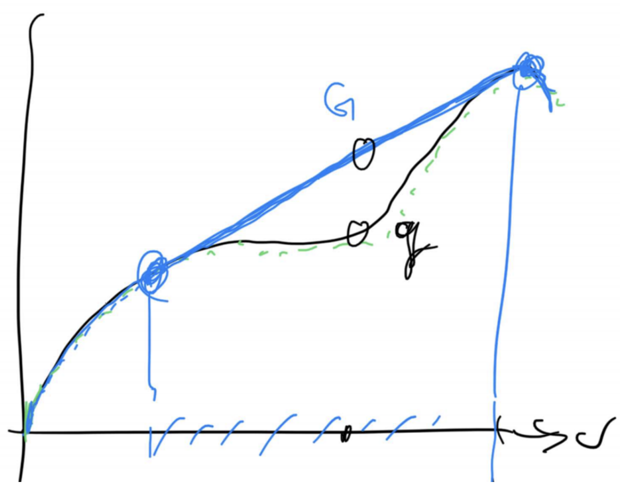
so

$$v\left(P + \frac{\alpha}{v^2}\right) = \frac{1}{\beta} = T.$$

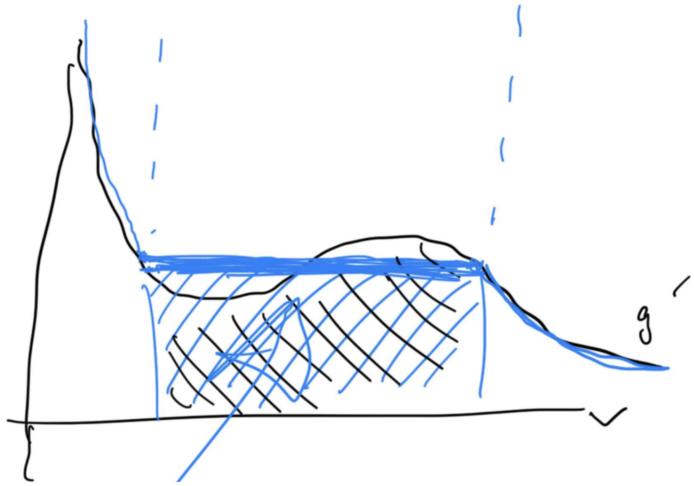
That is, we get van der Waal's equation,

$$v(P + \frac{\alpha}{v^2}) = NT.$$

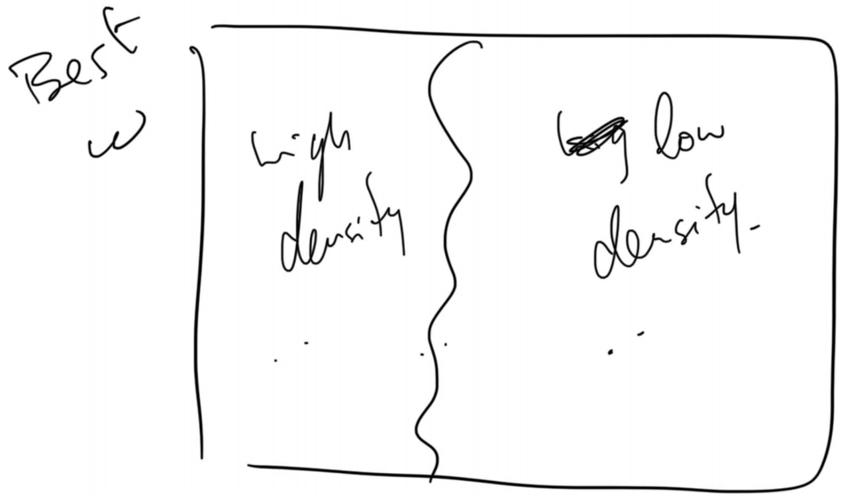
In the case of non-concavity, how do we fix it?



$P = \frac{\partial}{\partial v}[T \cdot G(v)]$, so let's graph g' and G', the derivative of the concave envelope.



Inside this shaded region above, recall which ρs carried most of the mass in $\widehat{Z}_n^r = \sum_\rho \exp(n^3 W(\rho) - \beta \widehat{\Phi}_n^r(\rho))$. Our analysis told us this, i.e. which micro configurations carry most of the mass in the canonical ensemble. This means that the best ω have regions of high density and regions of low density:



That is, the substance separates into a high density region (liquid) and a low density region (gas). For example, some of the water in a glass of water will evaporate into water vapor. Thus, van der Waal's equation correctly predicts the existence of a phase transition between gas and liquids.