The liquid-vapor phase transition in a system with a finite but coarse-grained attraction

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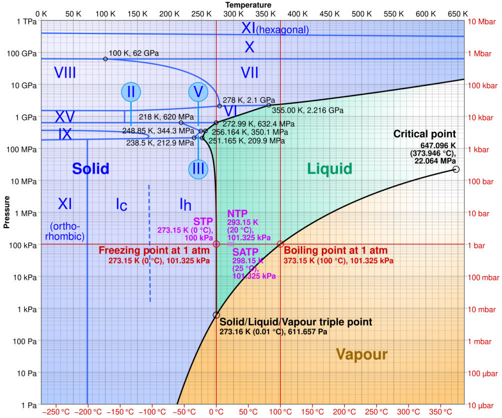
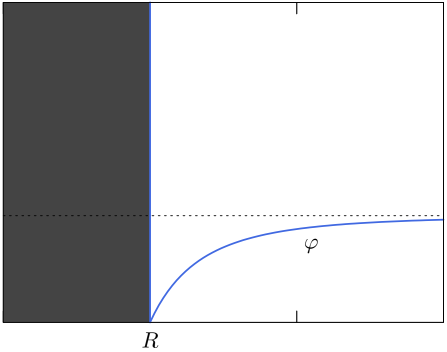
Phase diagram of water



The Van der Waals model

- Model: interaction potential: hard-core plus attractive φ:



The Van der Waals equation of state

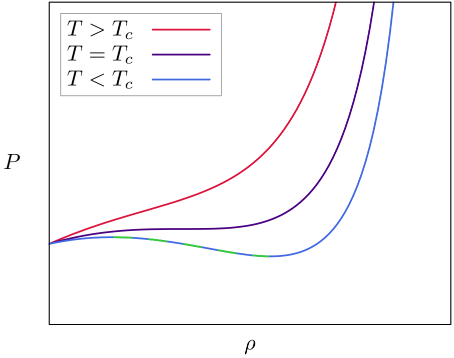
- Van der Waals: heuristic computation:

$$P(\rho) = \frac{T\rho}{1-\rho} + \frac{1}{2}\rho^2 \int dy\ \varphi(|y|)$$

  where

  - ρ: density
  - P: pressure
  - T: temperature

Pressure



- When the pressure is decreasing, the system is unstable. (Squeezing lowers the pressure!)

Free energy

- The free energy f solves

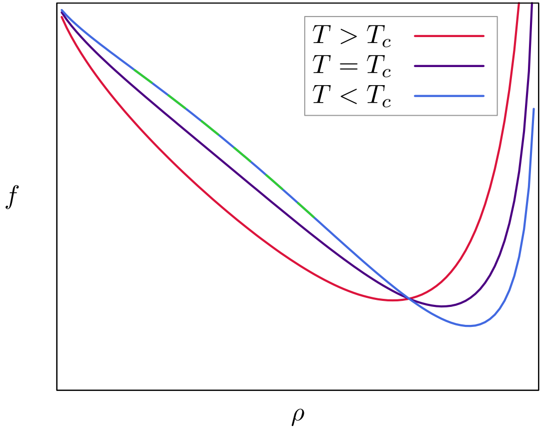
$$\frac{\partial^2 f}{\partial \rho^2} = \frac{1}{\rho}\frac{\partial P}{\partial \rho}$$

- Following Van der Waals,

$$f = T\rho \log\left(\frac{\rho e^{-1}}{1-\rho}\right) + \frac{1}{2}\rho^2 \int_{|y|>R} dy\ \varphi(|y|)$$

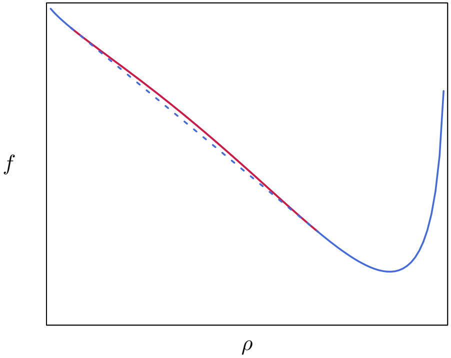
- The pressure is decreasing if and only if f is concave.

Free energy



Maxwell double tangent construction

- Idea: take the convex envelope of f:



The Lebowitz-Penrose theorem

- [Lebowitz, Penrose, 1966], [Kac, Uhlenbeck, Hemmer, 1963] Hard-core plus attractive interaction $\gamma^d\varphi(\gamma x)$.
- Take the limit $\gamma \to 0$.
- In other words, the attraction is of infinite range and infinitely weak (mean-field).
- **Theorem** [LP66]: f_0: free energy without the attraction, if $\gamma \to 0$,

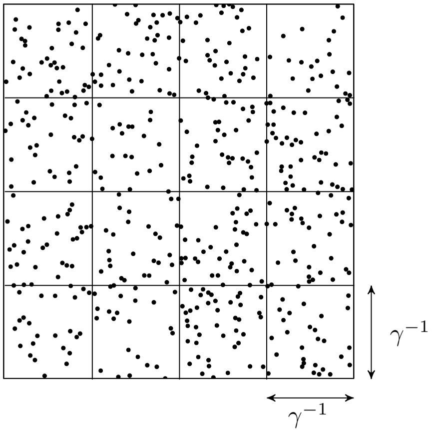
$$f(\rho) = \mathrm{CE}\left(f_0(\rho) + \frac{1}{2}\rho^2 \int \varphi\right)$$

In particular, there is a phase transition when $f_0 + \frac{1}{2}\rho^2 \int \varphi$ is not convex.

Finite γ

- Open problem: existence of a phase transition for $0 < \gamma \ll 1$.
- [Lebowitz, Mazel, Presutti, 1999] [Presutti, 2009]: Proved a phase transition at $0 < \gamma \ll 1$ by adding a four-body long-range repulsion.
- Our result: prove a phase transition in a model with a pair interaction. The interaction we consider is a coarse-grained version of a more realistic interaction.

The Box model



The Box model

- We coarse-grain the attraction on mesoscopic boxes of size γ^{-1}.
- We ignore the repulsion between different boxes.
- In other words, the interaction becomes

$$u_\gamma(x-y) = \begin{cases} \text{hard core}(x-y) - J_1\gamma^d & \text{if } \text{Box}_\gamma(x) = \text{Box}_\gamma(y) \\ -J_2\gamma^d & \text{if } \text{Box}_\gamma(x) \text{ is next to } \text{Box}_\gamma(y) \\ 0 & \text{otherwise} \end{cases}$$

- The probability of a configuration $x_1, \cdots, x_N$ is proportional to

$$e^{-\beta \sum_{i<j} u_\gamma(x_i - x_j) + \beta\lambda N}.$$

λ: chemical potential.

The Box model as a spin model

- The box model is equivalent to a nearest-neighbor spin model on the lattice $\mathbb{Z}^d$, where each vertex of $\mathbb{Z}^d$ corresponds to a box, and the spin value η_i corresponds to the density of particles in the box.
- The Hamiltonian for the spin model is

$$H = \gamma^{-d} \left(-\frac{1}{2} J_1 \sum_i \eta_i^2 - J_2 \sum_{i \sim j} \eta_i \eta_j + \sum_i f_\gamma(\eta_i) - \lambda \sum_i \eta_i \right)$$

where $f_\gamma(\eta)$ is the specific free energy for a system of hard-core particles in a box of size γ^{-1}.

The free energy in a box

- The free energy f_γ in a box with $N \equiv \eta\gamma^{-d}$ particles of radius R is

$$f_\gamma(\eta) := -\frac{1}{\beta\gamma^{-d}} \log \frac{1}{N!} \int_{([0,\gamma^{-1})^d)^N} dx_1 \cdots dx_N \prod_{i<j} \mathbb{1}_{|x-y|>2R}$$

- (We can be more general and just assume that f_γ is the free energy for any system of particles in a box interacting via a superstable and tempered potential.)
- (Our result is actually even more general, and allows for a large class of functions f_γ.)

Main result

- **Theorem**: If
$$f_0(\rho) - \frac{1}{2}(J_1 + 2dJ_2)\rho^2$$
is non-convex, then there exists $\gamma_0 > 0$ such that for all $\gamma \leqslant \gamma_0$, there exists a chemical potential λ at which the box model admits two distinct translation invariant Gibbs measures that differ in their value of the density.
- Thus, in this case, there is a first-order phase transition at λ.
- $f_0(\rho) = \lim_{\gamma\to 0} f_\gamma(\rho)$, so the condition for the existence of a phase transition is the same as for the Lebowitz-Penrose theorem.

Some comments on the proof

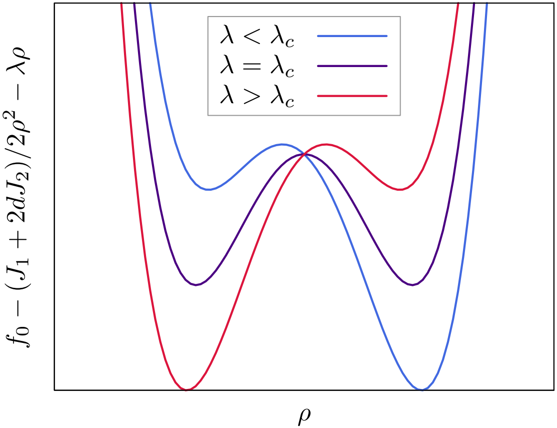
- The spin formulation of the box model is reflection-positive.
- Reflection-positivity (which means that $\mathbb{E}(f\theta f) \geqslant 0$ for any f and any reflection θ) is a very special property, but it is central to the argument. Our proof thus does not extend to non-coarse-grained models.
- On the other hand, using the tools of reflection-positivity, the proof is fairly easy.
- Next main idea: use the Dobrushin-Shlosman criterion, whose assumptions are proved using the reflection positivity.

The Dobrushin-Shlosman criterion

- [Dobrushin, Shlosman, 1981]
- Idea: if there are two disjoint events E_1, E_2 such that $\mathbb{P}_\lambda(E_1 \cup E_2)$ is large, and if for small λ, $\mathbb{P}_\lambda(E_1)$ is large and for large λ, $\mathbb{P}_\lambda(E_2)$ is large, then there is an intermediate value of λ where two phases coexist, one favoring E_1 and the other favoring E_2.
- Using reflection-positivity, we get bounds on $\mathbb{P}_\lambda(E_i)$ in terms of local considerations, involving the minimization of

$$f_0(\rho) - \frac{1}{2}(J_1 + 2dJ_2)\rho^2 - \lambda\rho.$$

The Dobrushin-Shlosman criterion



Conclusion and outlook

- We have proved a liquid-vapor phase transition in a system with a pair interaction.
- However, our proof relies on reflection positivity, and requires the interaction to be simplified (coarse-grained).
- On the other hand, using reflection positivity makes the proof rather easy, so the box model serves as a good toy model for the liquid-vapor phase transition.
- Open problem: what about the more realistic interaction $\gamma^d \varphi(\gamma x)$? Can the coarse-graining be shown to be a good approximation? (This is what is done in [Presutti, 2009] in the presence of a 4-body repulsion.)