Lecture 5: Ornstein-Zernike equation and condensation.

Recap: Density-density correlation functions.

$$\rho(\vec{r}) = \left\langle \sum_{i=1}^{N} \delta(\vec{r}-\vec{r}_i) \right\rangle$$

Note: $\langle \dots \rangle$ depends on ensemble!

$$\rho^{(2)}(\vec{r},\vec{r}\,') = \left\langle \sum_{j\neq i} \sum_{i=1}^{N} \delta(\vec{r}-\vec{r}_i)\,\delta(\vec{r}\,'-\vec{r}_j) \right\rangle$$

For homogeneous isotropic system: $\rho^{(2)}(\vec{r},\vec{r}\,') = \rho^2 g(|\vec{r}-\vec{r}\,'|)$

Radial distribution function $g(r) \Rightarrow$ conditional probability
potential of mean force.

Short-range correlations determine complete thermodynamics of the system

$$\boxed{\begin{aligned}
&\bullet\ \frac{U}{V} = \frac{3}{2}\rho k_B T + \frac{\rho^2}{2}\int d\vec{r}\, g(r)\, v(r) && \text{(Caloric route)}\\
&\bullet\ p = \rho k_B T - \frac{\rho^2}{6}\int d\vec{r}\, r\, g(r)\, v'(r) && \text{(Virial route)}\\
&\bullet\ 1+\rho\int d\vec{r}\,[g(r)-1] = \rho k_B T \kappa_T && \text{(Compressibility route)}
\end{aligned}}$$

The compressibility sum rule is more compactly rephrased as

$$\int d\vec{r}\, G(r) = \rho^2 k_B T \kappa_T \quad (*); \quad G(\vec{r},\vec{r}\,') = \langle \delta\hat{\rho}(\vec{r})\,\delta\hat{\rho}(\vec{r}\,')\rangle$$

$$\delta\hat{\rho}(\vec{r}) = \hat{\rho}(\vec{r}) - \langle\hat{\rho}(\vec{r})\rangle.$$

Compare with: $\tilde{G}(\vec{k}) = \int d\vec{r}\, G(\vec{r})\, e^{-i\vec{k}\cdot\vec{r}}$ (homogeneous + isotropic)

Define $\tilde{G}(k) = \rho S(k)$

$\Rightarrow$ $(*)$ can be rewritten as: $\boxed{\lim_{k\to 0} S(k) = \rho k_B T \kappa_T}$ $\rightarrow$ Slides

$S(k)$ is called the static structure factor (= measurable quantity!)

Ornstein-Zernike (OZ) integral equation

Define the indirect correlation function: $h(r) = g(r) - 1$

Note that $h(r) \to 0$ for $r \to \infty$ (uncorrelated particles).

The indirect correlation function satisfies the integral equation:

$$h(r) = c(r) + \rho \int d\vec{r}\,' \, c(|\vec{r} - \vec{r}\,'|) \, h(r').$$

(for now this relation <u>defines</u> $c(r)$.)

↳ can be derived using DFT

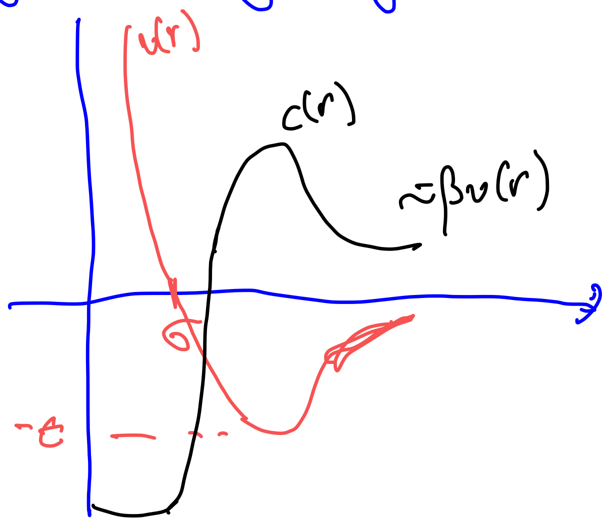
↳ direct correlation function

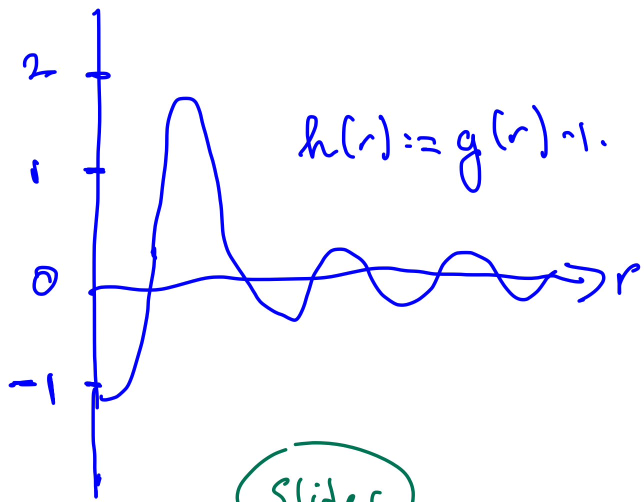
Dyson-like equation.

"More directly related to interaction potential since $c(r) \sim -\beta v(r)$ $(r \to \infty)$.

$c(r)$ does not contain any oscillations unlike $h(r)$.

E.g. Lennard-Jones fluid:





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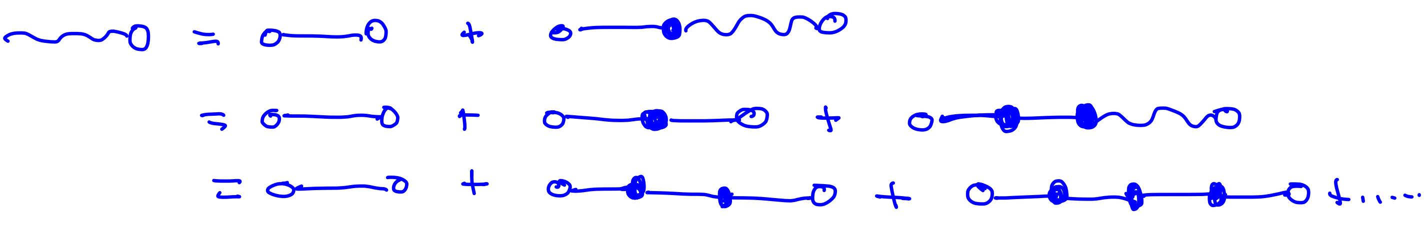
Iteration of OZ equation:

$$h(r_{12}) = c(r_{12}) + \rho \int d\vec{r}_3 \, c(r_{13}) \left[c(r_{32}) + \rho \int d\vec{r}_4 \, c(r_{34}) c(r_{42}) + \dots \right]$$

Diagrammatically:



Looks easier in Fourier space!

$$\tilde{h}(k) = \tilde{c}(k) + \rho\,\tilde{c}(k)\,\tilde{h}(k) \quad \Rightarrow \quad \tilde{h}(k) = \frac{\tilde{c}(k)}{1-\rho\,\tilde{c}(k)}$$

Or since $S(k) = 1 + \rho\,\tilde{h}(k)$ $\quad S(k) = \dfrac{1}{1-\rho\,\tilde{c}(k)}$ (Interpretation in terms of structure factor)

So from OZ equation, we can determine $g(r)$ if $c(r)$ is known!

random phase approximation

$\Rightarrow$ We need a closure relation. E.g. RPA $c(r) = -\beta v(r)$.
(soft core systems).

No exact way to obtain a closure relation $\Rightarrow$ approximative closure relations.

(see lecture notes for some examples)

For now, let's focus on one more approximative closure relation:

$$c_{PY}(r) = \{1 - e^{\beta v(r)}\}\, g_{PY}(r).$$

Excellent approximation for hard spheres.

For hard spheres, one can determine within PY closure an analytical solution for the direct correlation function:

$$c_{PY}(r) = \begin{cases} \dfrac{-(1+2\eta)^2 + 6\eta\left(1+\frac{1}{2}\eta\right)^2\left(\frac{r}{\sigma}\right) - \frac{1}{2}\eta(1+2\eta)^2\left(\frac{r}{\sigma}\right)^3}{(1-\eta)^4} & (r<\sigma) \\ 0 \quad (r>\sigma) & \end{cases}$$

(follows from OZ equation).

Note: Straightforward to obtain $S(k)$ via Fourier transformation.
However for $g(r)$: numerical calculations.

PY closure approximation is quantitative up until HS freezing, Although $g_{PY}(r)$ is not analytically available we can still obtain analytical results using compressibility or virial route:

$$\frac{\beta p_c}{\rho} = \frac{1+\eta+\eta^2}{(1-\eta)^3} \qquad \frac{\beta p_v}{\rho} = \frac{1+2\eta+3\eta^2}{(1-\eta)^2}.$$

$\Rightarrow$ Consistent up until $\mathcal{O}(\rho^4)$.

$\Rightarrow$ Inconsistency due to PY approximation.

Interestingly : $\boxed{p_{CS} = \frac{2p_c + p_v}{3}}$

Note: $g(r) \approx e^{-\beta v(r)}$ (dilute system).

$\Rightarrow$ Big difference between hard spheres and e.g. L.J system.

However, for dense systems $g_{HS}(r)$ is almost indistinguishable from $g_{PY}(r)$!

$\Rightarrow$ In dense system short-range repulsions dominate the short-range correlations

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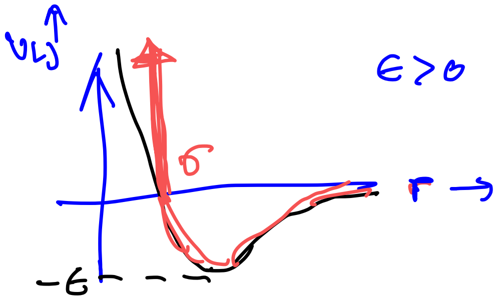
The gas-liquid phase transition.

Let's have a look at a simple model with attractions.

Consider the Lennard-Jones potential:



$\epsilon > 0$

$$v_{LJ}(r) = +4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

We approximate:

$$v_{LJ}(r) \approx \begin{cases} v_{HS}(r) & r < \sigma \\ -4\epsilon\left(\frac{\sigma}{r}\right)^6 & r > \sigma \end{cases}$$

σ: LJ parameter.

The free energy density can be written as

$$f(\rho,T) = f_{HS}(\rho) - \frac{\rho^2}{2} k_B T \int d\vec{r} \left[e^{-\beta v_{att}(r)} - 1 \right].$$

$$\approx f_{HS}(\rho) - \frac{\rho^2}{2} \int d\vec{r}\, 4\epsilon \left(\frac{\sigma}{r}\right)^6 =: f_{HS} - a\rho^2.$$

with $a = 16\epsilon v_0$ $\quad v_0 = \frac{\pi}{6}\sigma^3$

could be approximated by Carnahan-Starling but here we do a simpler approximation.

Consider configurational integral:

$$Q_{HS}(N,V,T) = \int d\vec{r} \exp\left[-\beta \sum_{i<j} v_{HS}(r_{ij})\right]$$

$$= V(V - 8v_0)(V - 2\cdot 8v_0)\cdots(V-(N-1)8v_0) \approx V^N\left(1 - \frac{N^2}{2}\frac{8v_0}{V} + \ldots\right)$$

$$\approx \left(V - \frac{N}{2} 8 v_0\right)^N =: (V - Nb)^N \quad (8v_0 << V).$$

binomial

We thus find the Helmholtz free energy density

$$\beta f(\rho) = \rho\left[\log\left(\frac{\rho\Lambda^3}{1-b\rho}\right) - 1\right] - \beta a \rho^2.$$

Van der Waals approximation.

$$p = -f + \rho\left(\frac{\partial f}{\partial \rho}\right)_T = \frac{\rho k_B T}{1-\rho b} - a\rho^2.$$

Derived by VdW without knowing the existence of atoms and molecules.

Recall thermodynamic stability criteria:

$$\left(\frac{\partial I_i}{\partial X_i}\right)_{X_1,\ldots X_{i-1}, X_{i+1},\ldots X_r, I_{r+1},\ldots I_n} \geq 0$$

with I_i and X_i conjugate.

I_i : intensive variables $\quad X_i$: extensive variables.

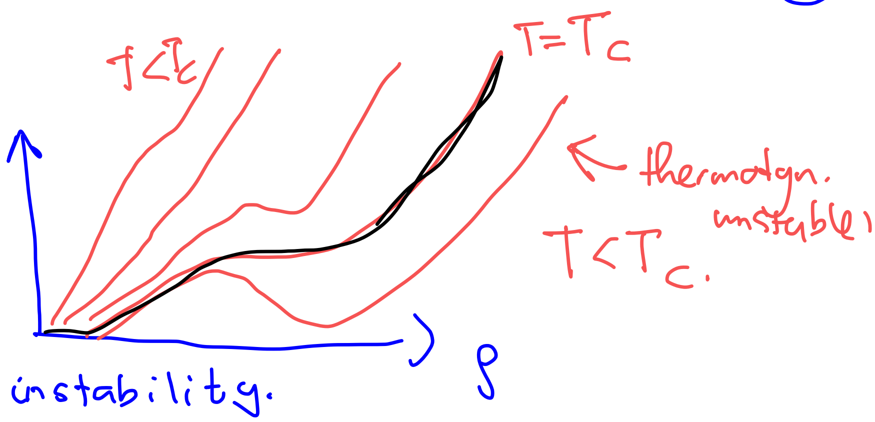
One such thermodynamic stability criterion is $-\left(\frac{\partial p}{\partial V}\right)_{N,T} \geq 0$

(positive isothermal compressibility)

in other words $\left(\frac{\partial p}{\partial \rho}\right)_T \geq 0$

However, for vdW gas we have a parameter regime for which $\left(\frac{\partial p}{\partial \rho}\right)_T < 0$

$\Rightarrow$ Thermodynamic instability.



At $T = T_c$ we have an inflection point in the pressure

$$\left(\frac{\partial p}{\partial \rho}\right)_T = 0 \;;\; \left(\frac{\partial^2 p}{\partial \rho^2}\right) = 0 \quad \text{at the critical point } (\rho_c, T_c).$$

Example, for vdW model: $\rho_c b = \frac{1}{3}$; $k_B T_c = \frac{8a}{27b}$. $\rightsquigarrow$ critical behaviour, critical exponents.

More generally the thermodynamic stability criterion says:

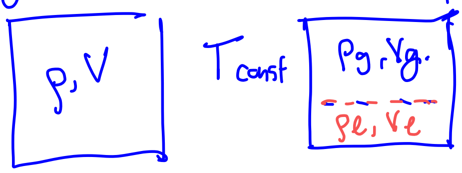
$$\left(\frac{\partial p}{\partial \rho}\right)_T > 0 \quad \overset{p = -f + \left(\frac{\partial f}{\partial \rho}\right)_T \rho}{\Longrightarrow} \quad \left(\frac{\partial^2 f}{\partial \rho^2}\right)_T \geq 0$$

$\Rightarrow$ free energy density isoterms should be a convex function of ρ.

Locus of all points $\rho(T)$ for which $\left(\frac{\partial^2 f}{\partial \rho^2}\right)_T = 0$ defines the spinodal.

$\Rightarrow$ denotes limit of stability. Within spinodal system is absolutely unstable. (free energy density is concave)

We will now show for $T < T_c$ system can lower its total free energy by phase seperation.



Neglecting surface effects: $F_{ps} = V f_{ps} = V_\ell f(\rho_\ell) + V_g f(\rho_g)$.

In canonical ensemble: N, V fixed: $V = V_\ell + V_g$.

$$\rho V = \rho_g V_g + \rho_\ell V_\ell.$$

Hence, we find using these constraints that

$$f_{ps} = \frac{V_\ell}{V} f(\rho_\ell) + \frac{V_g}{V} f(\rho_g) = \frac{V_\ell}{V} f(\rho_\ell) + \frac{V - V_\ell}{V} f(\rho_g)$$

$$= f(\rho_g) + \frac{V_\ell}{V}\left[f(\rho_\ell) - f(\rho_g)\right]$$

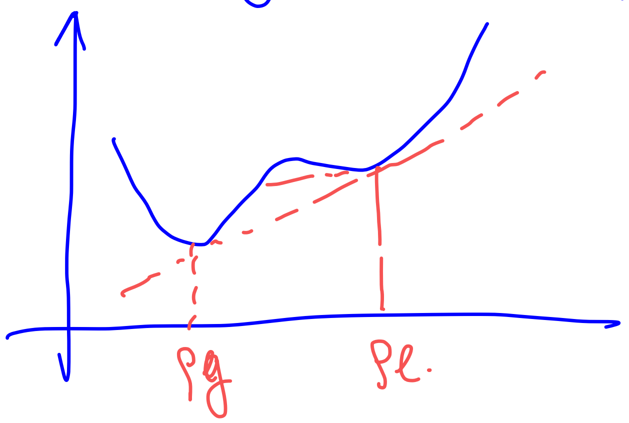
$$\rho V = \rho_g (V - V_\ell) + \rho_\ell V_\ell.$$
$$= \rho_g V + (\rho_\ell - \rho_g) V_\ell.$$

In other words: $\dfrac{V_l}{V} = \dfrac{\rho-\rho_g}{\rho_l-\rho_g}$.

Therefore:

$$f_{ps}(\rho,T) = f(\rho_g,T) + \frac{\rho-\rho_g}{\rho_l-\rho_g}\left[f(\rho_l,T)-f(\rho_g,T)\right] \qquad \rho_g \le \rho \le \rho_l, \quad T < T_c$$

(ρ_l, ρ_g) determined by minimisation of F_{ps}.



$\Rightarrow$ common tangent construction.

$$\left(\frac{\partial f}{\partial \rho}\right)_{\rho=\rho_g} = \left(\frac{\partial f}{\partial \rho}\right)_{\rho=\rho_l} = \frac{f(\rho_l)-f(\rho_g)}{\rho_l-\rho_g} \qquad (*)$$

Note that first condition.

$$\mu(\rho_l,T) = \mu(\rho_g,T) \Rightarrow \left(\frac{\partial f}{\partial \rho}\right)_{T,\rho=\rho_g} = \left(\frac{\partial f}{\partial \rho}\right)_{T,\rho=\rho_l}.$$

$$p(\rho_l,T) = p(\rho_g,T) \qquad \left(\text{Recall } p = -f + \left(\frac{\partial f}{\partial \rho}\right)_T \rho\right).$$

$$-f_{ps}(\rho_l,T) + \rho_l\,\mu(\rho_l,T) = -f_{ps}(\rho_g,T)\;\rho_g\,\mu(\rho_g,T)$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = V\left(\frac{\partial f}{\partial \rho}\frac{\partial \rho}{\partial N}\right)_{V,T} = \left(\frac{\partial f}{\partial \rho}\right)_T.$$

Define: $\mu(\rho_l,T) = \mu(\rho_g,T) = \mu_{co}(T)$

Hence:

$$p(\rho_g,T) - p(\rho_l,T) = 0 \Rightarrow (\rho_g-\rho_l)\left[\mu_{co}(T) - \frac{f(\rho_l,T)-f(\rho_g,T)}{\rho_l-\rho_g}\right] = 0$$

(Second condition in (*)).

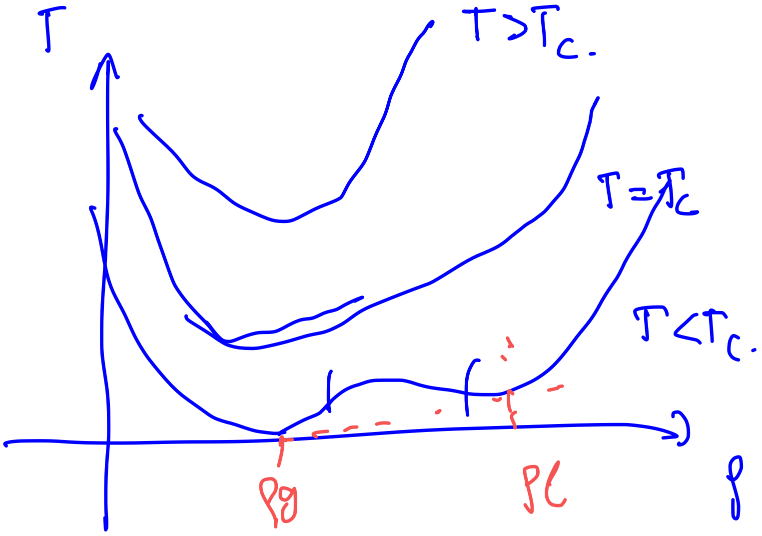
Common tangent construction $\Leftrightarrow$ equal chemical potential, equal pressure } both phases.

In general we have phase coexistence when all intensive variables in ~~both~~ all phases are equal.

So we have for $f(\rho, T)$

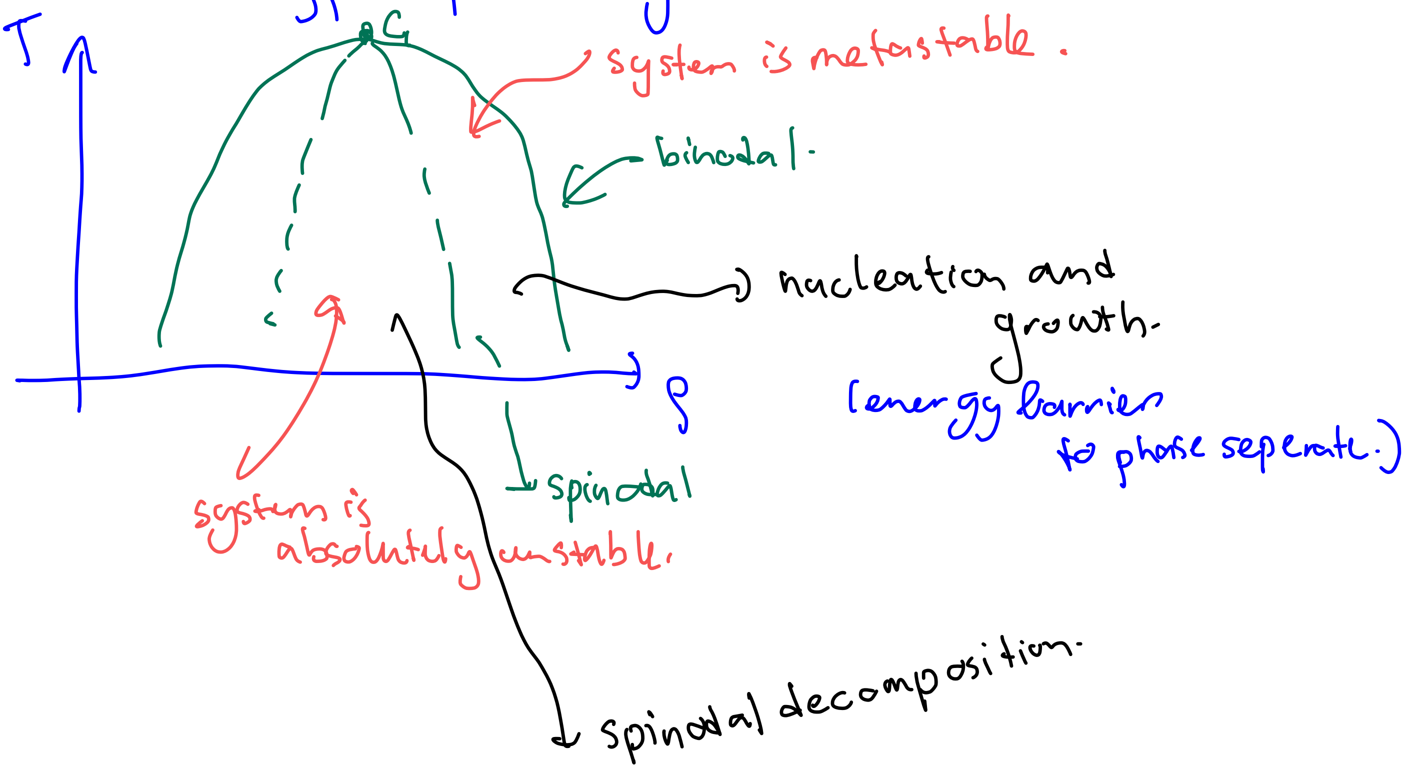
Note for $T > T_c$ no common tangent construction

$\Rightarrow$ system cannot lower its total free energy by phase separation.



$\rho_g(T)$ gas branch
$\rho_l(T)$ liquid branch
$\Big\} \rightarrow$ binodal.

We arrive at typical phase diagram:



Note that at critical point: $\lim_{q \to 0} S(q) = kT \left(\frac{\partial \rho}{\partial p}\right)_T \sim \langle N^2 \rangle - \langle N \rangle^2 \to \infty.$

Suppose incident wavelength $\lambda \sim 5000 \text{Å}$

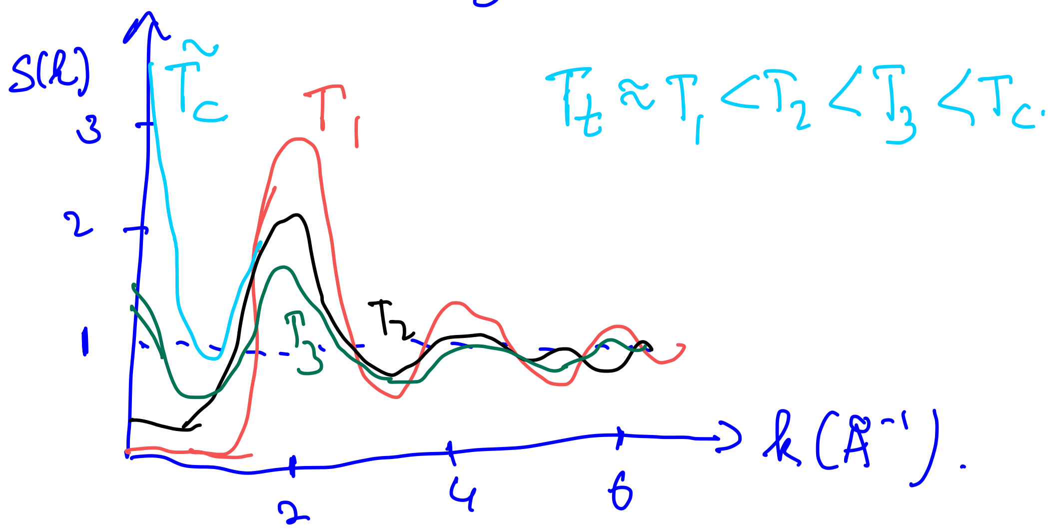
$\Rightarrow$ density fluctuations with $k < 2\pi/\lambda$ will scatter the light!

Close to critical point $I(\theta) \propto S(k)$ grows large!

$\Rightarrow$ Strong scattering gives rise to milky appearance.
(critical opalescense).

We shall show that this occurs when $\xi \sim \lambda$

Experimentally:



Originally OZ was developed for this!