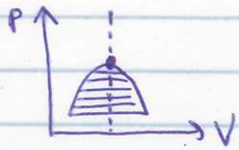
Macroscopic manifestations of a 2nd-order phase transition and connections with microscopic aspects of a critical behaviour

Recall

$\boxed{\text{Liquid / gas critical point}}$

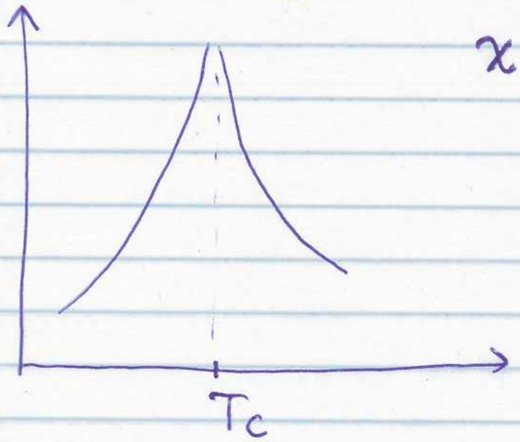


Magnetic system

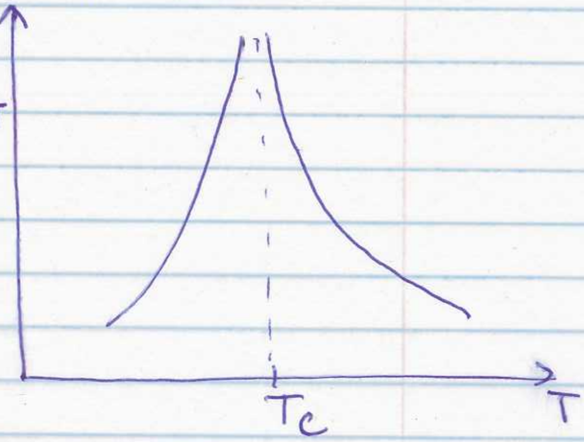
Isothermal compressibility diverges @ T_c

Spin susceptibility per site

$\varkappa \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$



$\chi \equiv \frac{1}{N}\left(\frac{\partial M}{\partial H}\right)_T$



tiny change Δp causes huge ΔV

tiny $\Delta H \Rightarrow$ huge ΔM

The system is "very soft" & unstable to external perturbations.
The system "cannot make up its mind" and therefore has large fluctuations

Small fluctuations for $T \gg T_c$ and $T \ll T_c$, but large and divergent ("macroscopic") fluctuations as $T \to T_c$

$T > T_c$ | $T = T_c$ | $T < T_c$

opaque

transparent | critical opalescence | transparent

Fluctuation – dissipation theorem: provides connection between (macroscopic) response functions like susceptibility or compressibility ("dissipation") and microscopic correlations ("fluctuation")

Consider Ising model for concretness

$$\underset{\substack{\text{susceptibility}\\\text{per spin}}}{\chi(T)} = \left(\frac{\partial m}{\partial H}\right)_T = \left(\frac{\partial \langle S_0 \rangle}{\partial H}\right)_T =$$

$\leftarrow$ arbitrary fixed site

$$= \frac{\partial}{\partial H}\left(\frac{\sum_{\{S_i\}} S_0\, e^{-\beta E_{int}(S_1, S_2, \ldots) + \beta H \sum_i S_i}}{\sum_{\{S_i\}} e^{-\beta E_{int}(S_1, S_2, \ldots) + \beta H \sum_i S_i}}\right) =$$

$$= \left\langle S_0 \beta \sum_i S_i \right\rangle - \frac{1}{Z^2} \mathrm{Tr}\left\{ S_0 e^{-\beta E_{tot}} \right\} \mathrm{Tr}\left\{ \beta \sum_i S_i\, e^{-\beta E_{tot}} \right\}$$

$$= \frac{1}{k_B T} \sum_i \Big(\underbrace{\langle S_0 S_i \rangle - \langle S_0 \rangle \langle S_i \rangle}_{\substack{|||\\ \Gamma(i) \,\equiv\, \text{"connected correlation function"}}} \Big)$$

(Connection with study of "fluctuations":

$$\boxed{\underset{\text{per spin}}{\chi(T)} = \frac{\langle M^2 \rangle - \langle M \rangle^2}{k_B T \cdot N}}$$

"dissipation" "fluctuation")

Thus,

$$\boxed{\chi(T) = \frac{1}{k_B T} \sum_i \Gamma(i) = \frac{1}{k_B T} \int d^d r\, \Gamma(\vec{r})}$$

arbitrary magnetic system on a lattice; no approximations — continuum description

$$\Gamma(\vec{r}) = \langle S_0 S_{\vec{r}} \rangle - \langle S_0 \rangle \langle S_{\vec{r}} \rangle$$

More generally, $\Gamma(r, r') = \langle S_r S_{r'} \rangle - \langle S_r \rangle \langle S_{r'} \rangle =$

$= \Gamma(r - r')$

for translationally invariant systems.

For fluid system

$$\varkappa(T) = \frac{1}{k_B T} \int d^d\vec{r}\; G(\vec{r})$$

isothermal compressibility

$$G(\vec{r}) \equiv \langle n(0)\, n(\vec{r}) \rangle - \langle n(0) \rangle \langle n(r) \rangle$$

$$n(\vec{r}) = \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i)$$

– density correlation fnctn (aka pair correlation fnctn)

<u>Remarks</u>: ✱ Expressions for χ, $\varkappa$ – examples of "fluctuation – dissipation" theorem, connecting microscopic correlations (fluctuation) with a macroscopic response function (dissipation)

✱ $\langle S_0 S_i \rangle$ – can interpret as measuring probability that if spin @ 0 is ↑ then spin @ i is ↑

= (probability both S_0 & S_i point in the same dir) − (probability S_0 & S_i point in opposite dirs.)

"measure of correlation"

If S_0 and S_i are completely uncorrelated, then

$\langle S_0 S_i \rangle = \langle S_0 \rangle \langle S_i \rangle$, and $\Gamma(i) = 0$

In the presence of interactions, spins become correlated. For example, for ferromagnetic interaction spins become positively correlated and $\Gamma(i) > 0$

* In order to get $\chi(T_c) = \infty$, we must have correlations @ T_c decaying more slowly than $\frac{1}{|\vec{r}|^{d+\epsilon}}$ at large $|\vec{r}|$:

otherwise $\int \Gamma(\vec{r}) d^d r < \int \frac{r^{d-1} dr}{r^{d+\epsilon}}$ = finite.

$\Rightarrow$ @ T_c, connected correlations are necessarily long-range power law.

Ornstein-Zernike law (correlations in the meanfield theory)

$T > T_c$ or $T < T_c$ $r \gg \xi$ $\Gamma(r) \sim \frac{e^{-r/\xi}}{r^{\frac{d-1}{2}}}$

$\xi(T \to T_c) \sim |T - T_c|^{-\nu}$, $\nu_{mf} = \frac{1}{2}$

$T = T_c$ (or $r \ll \xi$) $\Gamma(r) \sim \frac{1}{r^{d-2}}$

More generally: $\boxed{\Gamma(r) \sim \frac{1}{r^{d-2+\eta}}}$ for $r \ll \xi$

$\boxed{\eta_{mf} = 0}$ η ← modification due to fluctuations

$$\chi(T) \sim \int^{\xi(T)} \frac{r^{d-1} dr}{r^{d-2+\eta}} \sim \left(\xi(T)\right)^{2-\eta} \sim$$

$$\sim \left(|T - T_c|\right)^{-\nu \cdot (2-\eta)} \sim |T - T_c|^{-\gamma}$$

$$\boxed{\gamma = \nu \cdot (2 - \eta)}$$

meanfield: $\left.\begin{array}{l} \gamma_{mf} = 1 \\ \nu_{mf} = \frac{1}{2} \\ \eta = 0 \end{array}\right\}$ ✓

(*) **Scattering experiments effectively measure** Fourier transform of the density-density correlation function

For example, consider neutron in a medium

$$V(r) = \sum_i v_0\, \delta(\vec{r}-\vec{r}_i) = v_0\, n(r)$$

↑ neutron-nucleus interaction; very short-range

Scattering $\vec{k}_{initial} \longrightarrow \vec{k}_{final}$ is proportional to

*scattering from a "static $n(r)$" ("snapshot")

↑

OK for elastic scattering

$$\left| \underbrace{\langle \vec{k}_f \,|\, \hat{V} \,|\, \vec{k}_i \rangle}_{v_0 \int d^3\vec{r}\, e^{i(\vec{k}_i-\vec{k}_f)\cdot\vec{r}}\, n(\vec{r})} \right|^2 =$$

$$= v_0^2 \int d^3\vec{r}\, d^3\vec{r}\,'\, n(\vec{r})\, n(\vec{r}\,')\, e^{+i(\vec{k}_i-\vec{k}_f)\cdot(\vec{r}-\vec{r}\,')}$$

Averaging over many neutrons ~ averaging over possible states of the system ~ thermal average

Scattering rate for $\vec{q} = \vec{k}_f - \vec{k}_i$ $\quad \propto \int d^3\vec{r}\, d^3\vec{r}\,' \langle n(r)\, n(r')\rangle\, e^{-i\vec{q}\cdot(r-r')}$

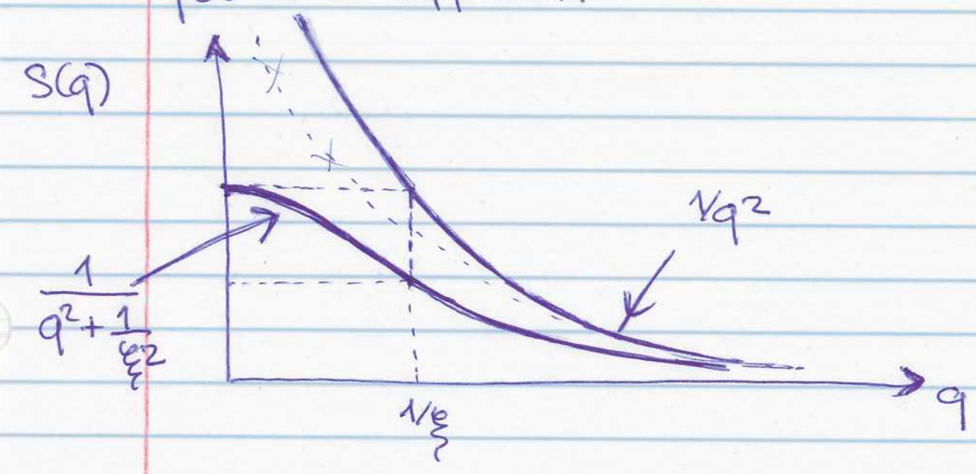
$$= \mathrm{Vol.} \underbrace{\int d^3r\, G(r)\, e^{-i\vec{q}\cdot\vec{r}}}_{S(\vec{q})}$$

$$S(\vec{q}) = \int d^3\vec{r}\; G(r)\, e^{-i\vec{q}\cdot\vec{r}}$$ – density-density **structure factor** in q-space

Ornstein – Zernike theory:

$$S(\vec{q}) \sim \frac{1}{\vec{q}^{\,2} + \frac{1}{\xi^2}}$$ – Lorentzian function of the wavenumber q.

The width of the Lorentzian $\sim \frac{1}{\xi} \to 0$ as the critical point is approach



⊛ Critical opalescence:

* "Macroscopic understanding" : $\varkappa \to \infty$ ⇒ strong fluctuations, regions of various sizes with different densities. Density variations on length scales of the same order as wavelength of the visible light will strongly scatter the light ⇒ the medium looks opaque.

* "Microscopic understanding" : light scattering is determined by $S(q \sim \frac{2\pi}{\lambda_{light}})$. At the critical point one has fluctuations on all wavelengths, in particular on scales $\sim \lambda_{light} \gg$ inter-particle spacing, and $S(q \sim \frac{2\pi}{\lambda_{light}})$ is large!