Mean Field Theory
and
Landau's MFT of Free Energy

Mini-talk 5

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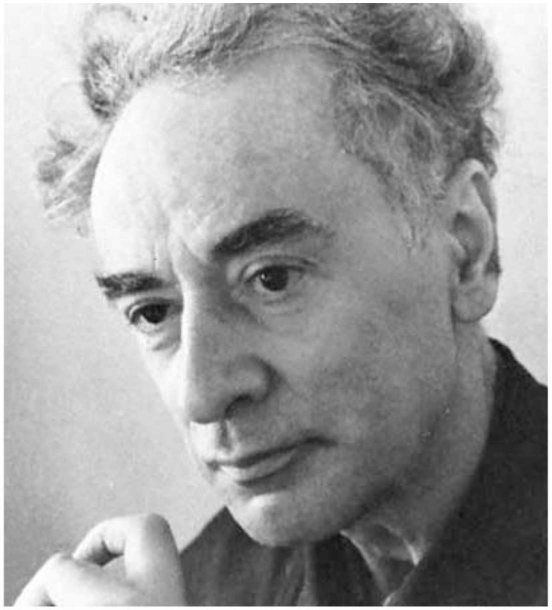
Agenda

- Mean Field Theory
  - History: van der Waal
  - 1D Ising model
  - Correlation function Theory
  - Critical opalescence Experiment
- Landau's
  - Free energy definition
  - Why significant advance in concept?
  - An example
- Validity of MFT
- Next time:

Notable Persons of the Week



Van der Waal
1837-1923

Landau
1908-1968

Notable Pictures of the Week

Lower Temperature
Broken Symmetry
Acquire correlation:
Micro interaction->
Macro behavior

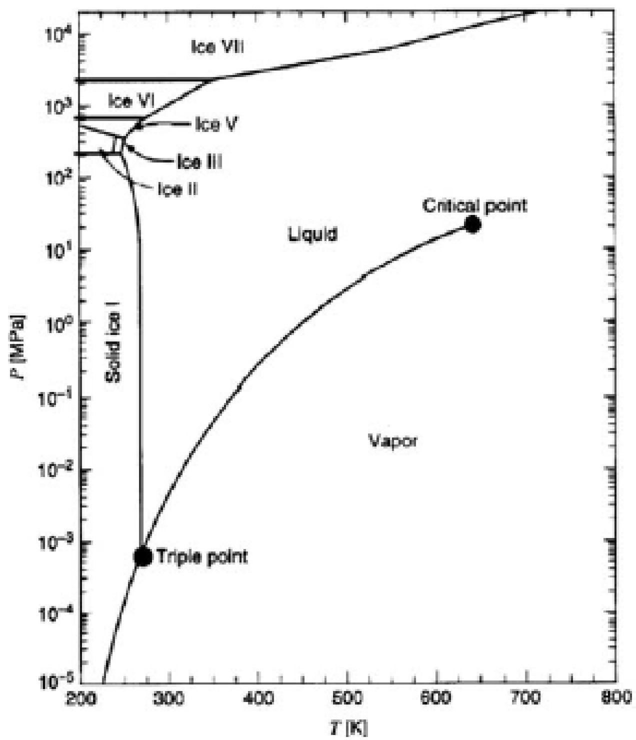
Kadanoff, 2010

Figure 1: Splash and snowflake. This picture is intended to illustrate the qualitative differences between the fluid and solid phases of water. On the left is liquid water, splashing up against its vapor phase. Its fluidity is evident. On the right is a crystal of ice in the form of a snowflake. Note the delicate but rigid structure, with its symmetry under the particular rotations that are multiples of sixty degrees.

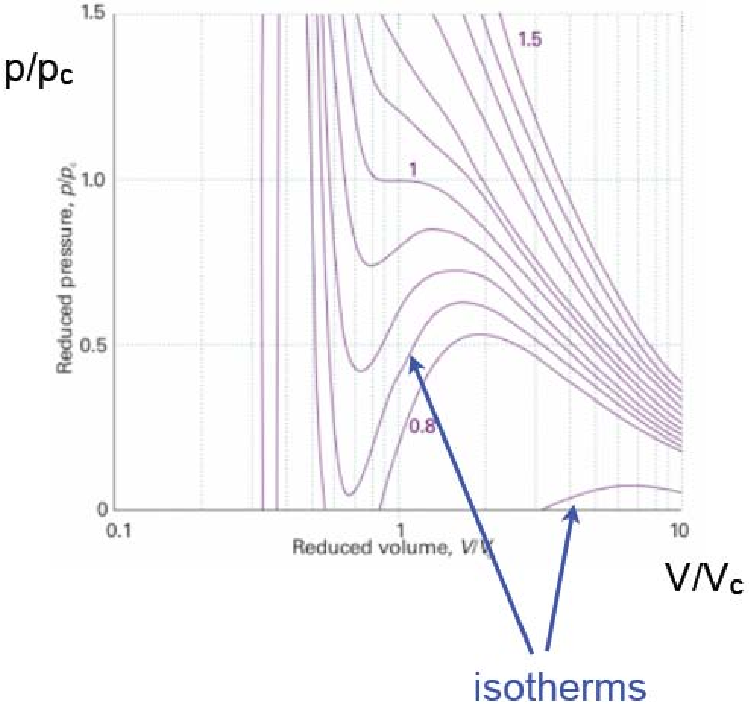
1. Qualitative difference: bifurcation, nonlinearity, singular or non-analytic?
2. Can brain or its function, modeled by phase transition?
3. What is its or their <m(r,t)>?

Mean Field Theory (MFT)

- Cubic in V
- Unstable? Metastable?

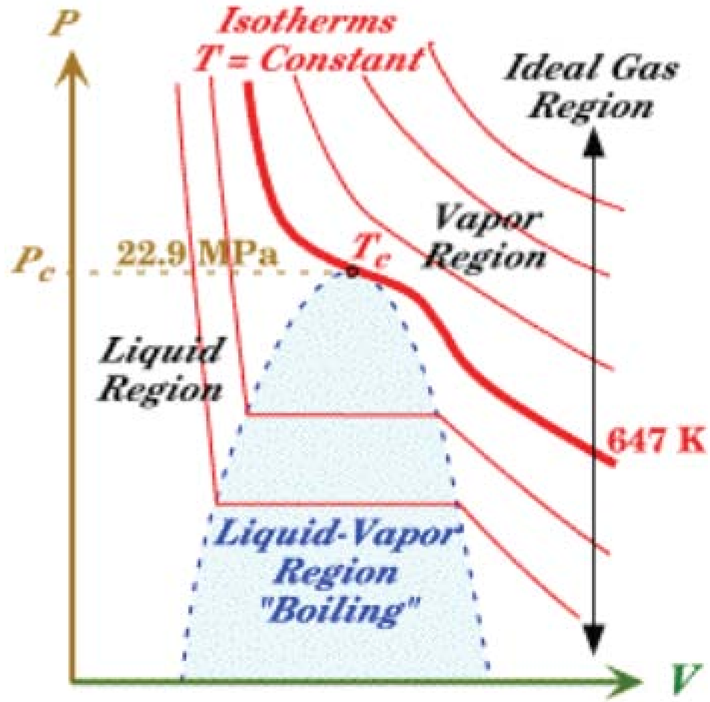


In 1873 van der Waals derives an approximate equation of state for fluids:



Maxwell Stabilized it

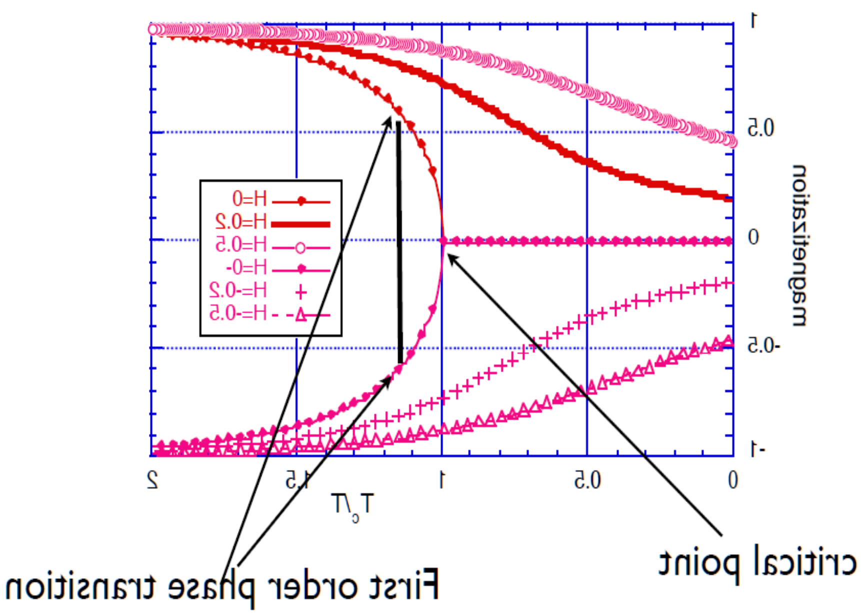
- Finite Δρ at isotherm
- Equal area rule



Cartoon P-V diagram for water but CO_2 is quite similar.

J.C. Maxwell Nature, **10** 407 (1874),**11** 418 (1875).

Fluids and Magnets



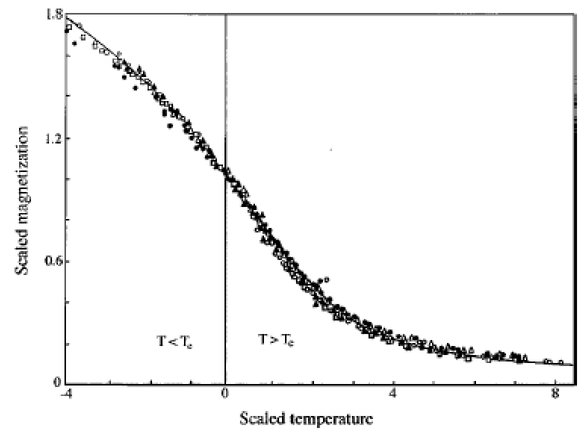


FIG. 1. Experimental *MHT* data on five different magnetic materials plotted in scaled form. The five materials are $CrBr_3$, EuO, Ni, YIG, and Pd_3Fe. None of these materials is an idealized ferromagnet: $CrBr_3$ has considerable lattice anisotropy, EuO has significant second-neighbor interactions. Ni is an itinerant-electron ferromagnet, YIG is a ferrimagnet, and Pd_3Fe is a ferromagnetic alloy. Nonetheless, the data for all materials collapse onto a single scaling function, which is that calculated for the $d=3$ Heisenberg model [after Milošević and Stanley (1976)].

Fluids and Magnet Data

Connection between fluids and single-axis magnets

order parameter:	ρ-ρ_c	versus	magnetization, $<\sigma>$
varied by changing	p	versus	magnetic field, h
other thermo variable	T	versus	T
	compressibility	versus	susceptibility, $\partial<\sigma>/\partial h$
jump=	boiling	versus	flip sign of $<\sigma>$

T.D. Lee and C.N. Yang. Statistical theory of equations of state and phase transitions: I. Theory of condensation. Phys. Rev., 87:404–409, 1952.

T.D. Lee and C.N. Yang. Statistical theory of equations of state and phase transitions: II. Lattice gas and Ising model. Phys. Rev., 87:410–419, 1952.

1D Ising Model MFT (I)

- *Single* magnetic moment μ *in* a magnetic field H
- *The* Hamiltonian or energy $E = -\mu\sigma H$
- *The* Boltzmann probability of finding $\sigma \sim e^{-\beta E}$
- *The* partition function, $Z \equiv \sum_{\{\sigma\}} e^{-\beta E} = \sum_{\{\sigma\}} e^{h\sigma} = 2\cosh(h)$

where $h \equiv \beta\mu H$

- $$< \sigma > \equiv \frac{1}{Z}\sum_{\{\sigma\}} \sigma e^{h\sigma} = \frac{1}{Z}\frac{\partial}{\partial h}\sum_{\{\sigma\}} e^{h\sigma} = \frac{\partial}{\partial h}\ln(Z) = \tanh(h)$$

Ising Model MFT (II)

- $Many\ spins, \sigma_r,\ in$ a magnetic field H and interacting with <nn>, $J_{rs} \equiv J$,
- The Hamiltonian $\hat{H} = -J \sum_{<nn>} \sigma_r \sigma_s - \mu H \sum_r \sigma_r$
- $Simplification: \ -\beta \hat{H} = K \sum_{<nn>} \sigma_r \sigma_s + h \sum_r \sigma_r$

$where$ $K = \beta J = J / kT$: coupling strength relative to thermal energy

- $Mean\ Field\ Theory \Rightarrow look$ at just σ_r,

on average, what is its interaction with the rest?

$$K \sum_{<s\ nn\ \text{of r}>} \sigma_s + h_r \simeq K \sum_{<s\ nn\ \text{of r}>} <\sigma_s> + h_r \simeq Kz <\sigma_r> + h_r \equiv h_{eff}$$

$where$ z=nn of r=coordinate number of site r; using single spin result $\Rightarrow$

for z=2, 4, and 6 for linear, square, and cubic lattice or

d=1,2, and 3 dimensions, respectively.

- $<\sigma_r> = \tanh(h_r + Kz <\sigma_r>)$

Ising Model MFT (III)

$<\sigma_r>= \tanh(h_r + Kz <\sigma_r>) \Rightarrow ?$

- Near critical point $\Rightarrow$ *No* h, small $<\sigma>$
- $\tanh(x) \sim x - x^3/3 + \ldots \Rightarrow$ *To* O(x)

$<\sigma>= Kz <\sigma> \Rightarrow Kz = 1 = K_c z$

- $Kz \equiv 1 - t \equiv 1 - \left(\frac{T - T_c}{T_c} \right) = \frac{T}{T_c}$

To O(x^3), including O(h) $\Rightarrow$ *a cubic equation*

$t <\sigma>= h - <\sigma>^3 /3$

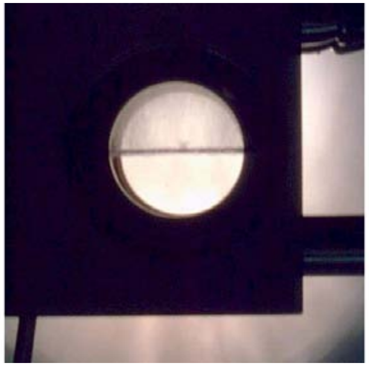
$\Rightarrow$ *All* qualitative but not quantitative *relations* ...

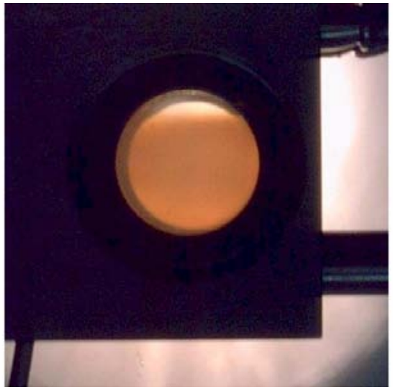
Next big Idea: Critical Opalescence

- T. Andrews (1869): clear fluids becomes cloudy
- Smoluchowski (1908), Einstein (1910)

  Density fluctuation become large at critical point and cause divergence in compressibility
- Ornstein and Zernike (1914)

  Not the size in fluctuation but the range of fluctuation region



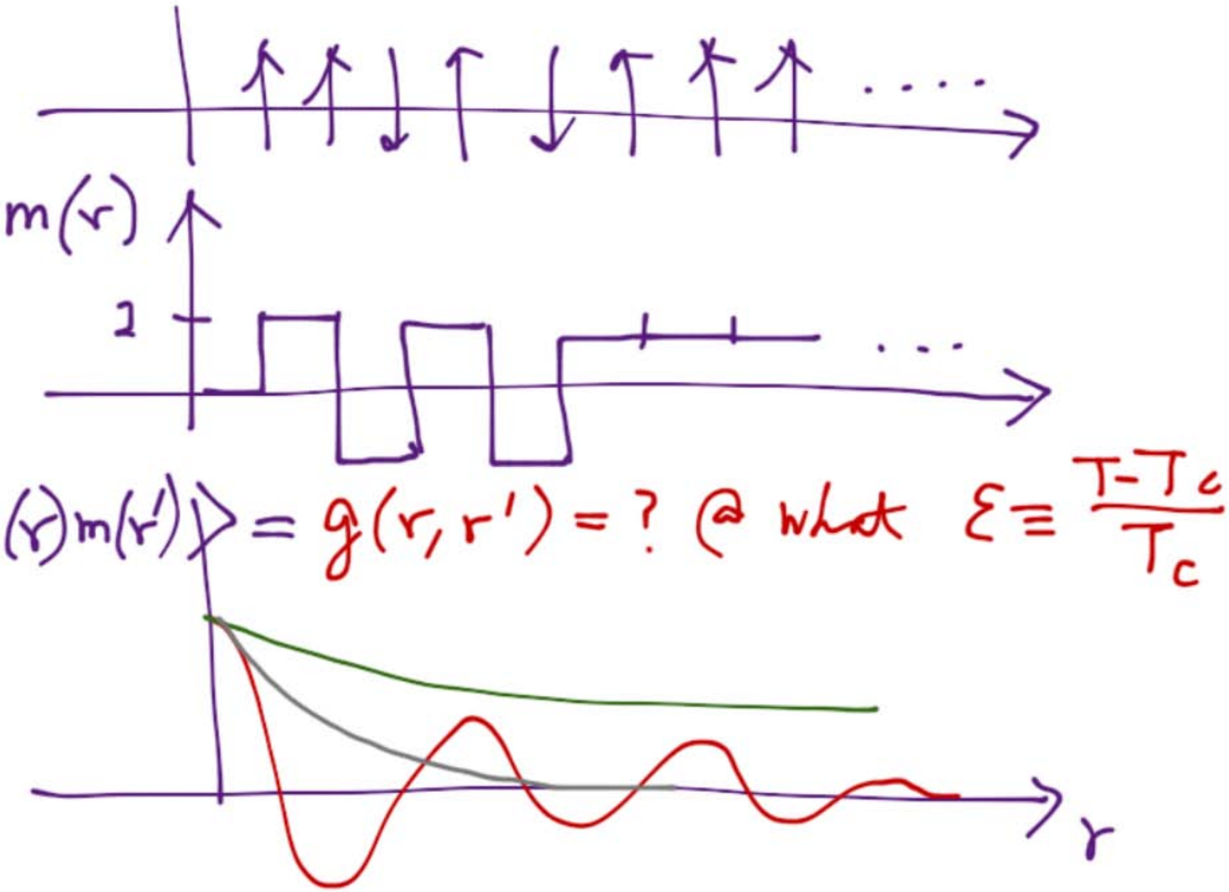


$$g(\vec{r},\vec{s}) \equiv <\left[\rho(\vec{r}) - <\rho>\right]\left[\rho(\vec{s}) - <\rho>\right]> =$$

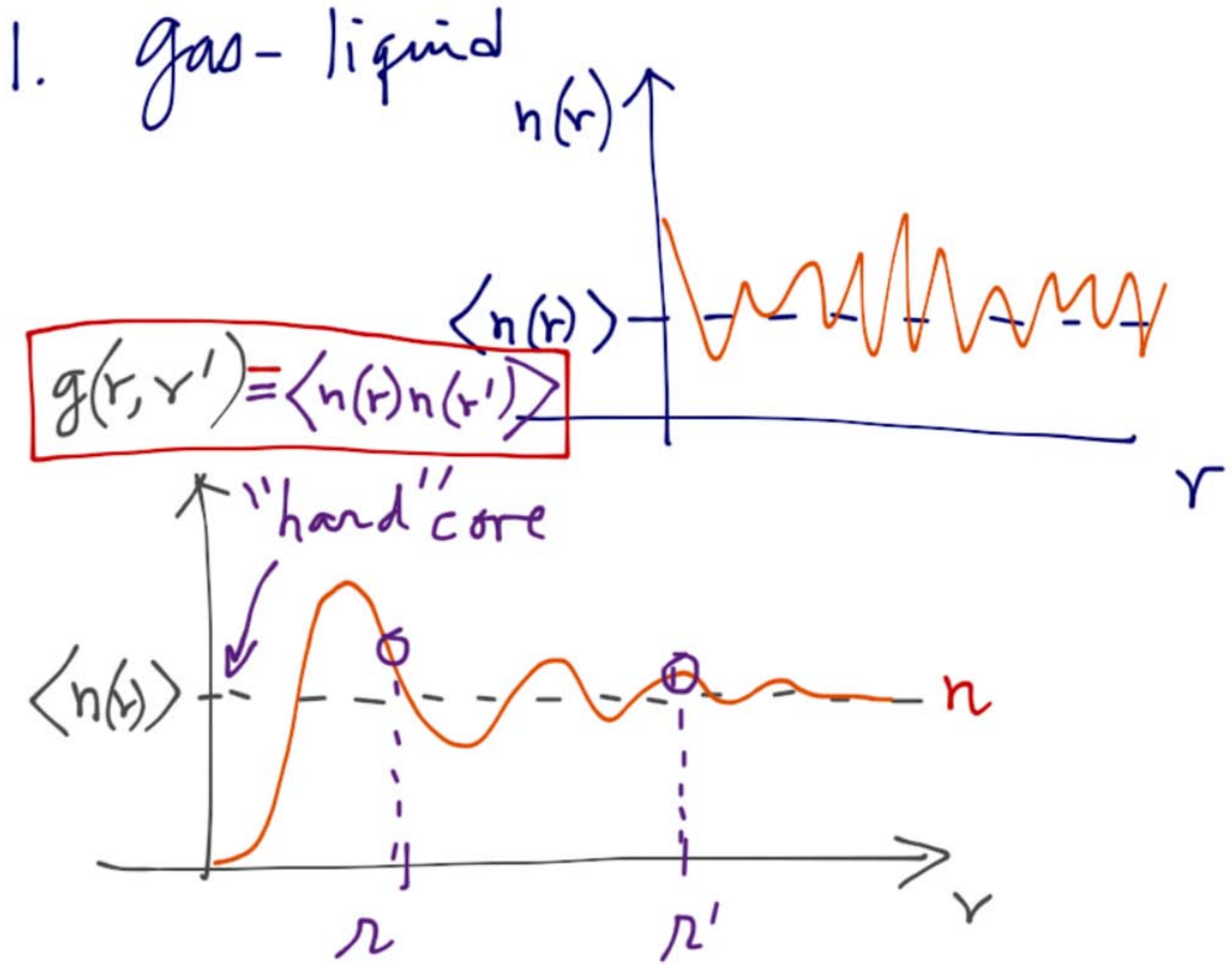
$$= \frac{\partial}{\partial h(\vec{s})} <\sigma(\vec{r})> = ?$$

Spatial Correlation Function

2. Magnetic system



Spatial Correlation Function



Time Correlation Function

3) Electrical conduction of charge.

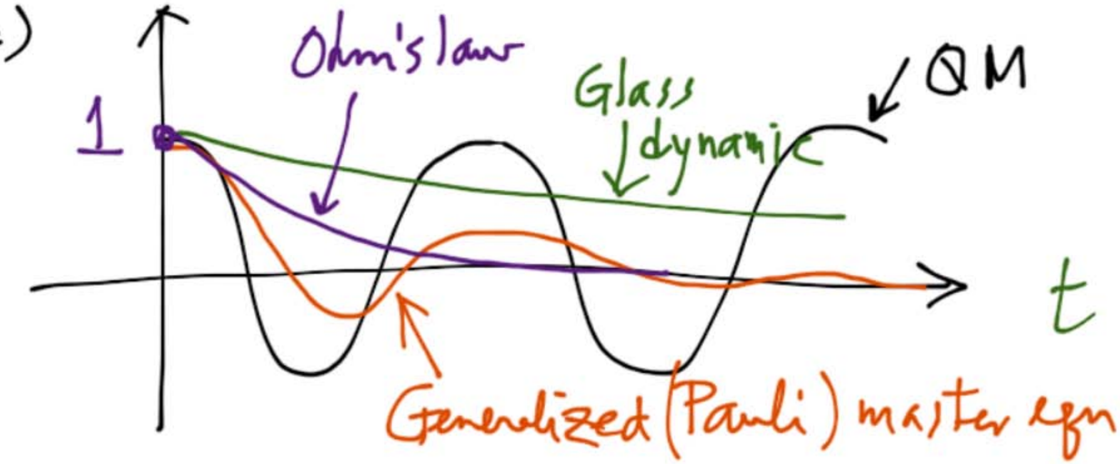
$i(t) \equiv q * v(t)$

(a) $v(t) = \langle v(t) \rangle + \varepsilon \eta(t)$

- $\varepsilon \ll 1$
- $\eta(t)$ noise

(b) $C(t,t') \equiv \langle v(t) v(t') \rangle = ?$

(c)



The answer is:

$$g(r,r') = \delta_{r,r'} + K \sum_{s\ <nn>} g(s,r') - 3 < \sigma_r >^2 g(r,r')$$

- Solved by *Fourier Transform*

$$g(\vec{r},\vec{r}\,') \equiv \int \frac{d^d\vec{k}}{(2\pi/a)^d} e^{i\vec{k}\bullet(\vec{r}-\vec{r}\,')} g(\vec{k})$$

$$\delta_{r,r'} \equiv \int \frac{d^d\vec{k}}{(2\pi/a)^d} e^{i\vec{k}\bullet(\vec{r}-\vec{r}\,')} 1$$

- $\kappa^2 \equiv t + < \sigma >^2; \ \xi \equiv \dfrac{a}{\kappa}$

$$g(\vec{r},\vec{r}\,') \sim \frac{1}{|r-r'|} e^{-\frac{|r-r'|}{\xi}}$$

Consequence is:

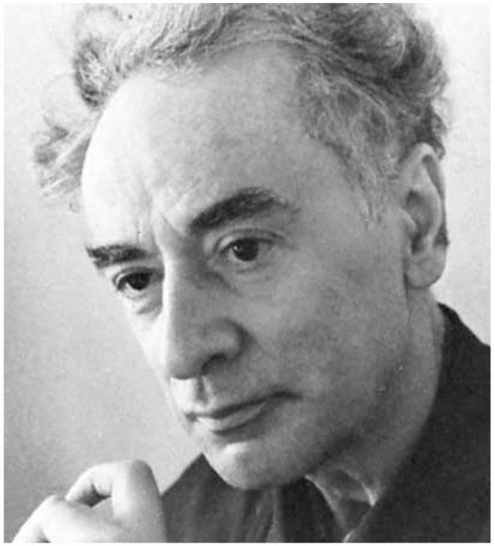
$$\kappa^2 \equiv t + <\sigma>^2;\ \xi \equiv \frac{a}{\kappa} \to \infty \ when\ T \to T_c$$

$$g(\vec{r}, \vec{r}\,') \sim \frac{1}{|r - r'|} e^{-\frac{|r-r'|}{\xi}} \to \frac{1}{|r - r'|},\ a\ power\ law$$

- Re*call* in nuclear physics, the Yukawa potential

Landau (~1937) Order Parameter Concept

- 1^{st} order Phase transitions
are manifestations of a Broken Symmetry of an
- Order parameter
    - fluid density, magnetization
    - measures the extent of symmetry breaking
- Spatial and time dependence implicates
    - Correlation (scattering experiments) and
    - Dimensionality (next time)



Universality?

- Ferromagnet
- Binary alloy
- Liquid-gas
- Surface adsorption
- Approximated models may be incorrect for critical phenomena

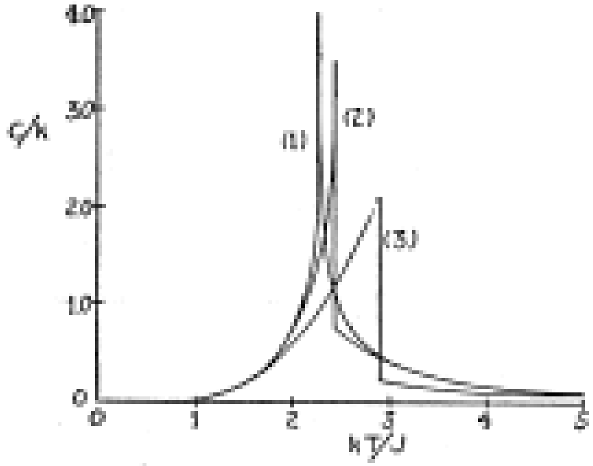


FIG. 1. The exact specific heat curve of the two-dimensional Ising lattice (curve 1) is compared with approximate curves of Kramer-Wannier (curve 2), and Bethe (curve 3) (see reference 5).

Universality

TABLE XI. Correspondences between lattice gas model and Ising model.

Ising model	Lattice gas model
Number of up spins	Number of molecules
Partition function	Grand partition function
Number of spins	Volume
Free energy minus magnetic field	Pressure
Magnetization	Density minus critical density
Specific heat C_m	Specific heat C_V

TABLE XII. Definitions of critical indices for liquid–gas transition. If this transition is described correctly by the lattice gas model, α, α', β, γ, γ', and δ all have the same values as in the Ising model.

ϵ	$\epsilon=(T-T_c)/T_c$	
α'	$C_v\sim(-\epsilon)^{-\alpha'}$	$\rho=\rho_c$, $\epsilon<0$
α	$C_v\sim\epsilon^{-\alpha}$	$\rho=\rho_c$, $\epsilon>0$
β	$(\rho_L-\rho_G)\sim(-\epsilon)^{\beta}$	$\epsilon<0$, coexistence curve.
γ'	$K_T\sim(-\epsilon)^{-\gamma'}$	$\epsilon<0$, coexistence curve.
γ	$K_T\sim\epsilon^{-\gamma}$	$\rho=\rho_c$, $\epsilon>0$
δ	$\lvert P-P_c\rvert\sim\lvert\rho-\rho_c\rvert^{\delta}$	$T=T_c$
μ	Surface tension $\sim(-\epsilon)^{\mu}$	$\rho=\rho_c$, $\epsilon<0$

Kadanoff et al, RMP 39, 395 (1967)

The Order Parameters

TABLE I. Partial list of transitions with critical points. In general, the symbol h denotes the conjugate to $\langle\phi\rangle$.

Transition	Meaning of $\langle\phi\rangle$	Free choice in $\langle\phi\rangle$	Thermodynamic conjugate of ϕ
Liquid–gas	$\rho-\rho_c$	$\phi>0$=liquid $\phi<0$=vapor (2 choices)	μ
Ferromagnetic	magnetization $\langle\mathbf{M}\rangle$	if n equivalent "easy axes" $2n$ choices	applied magnetic field, H, along easy axes
Heisenberg model ferromagnet	magnetization $\langle\mathbf{M}\rangle$	direction of $\langle\mathbf{M}\rangle$ [can choose any value on surface of sphere.]	$\mathbf{H}$
Antiferromagnet	sublattice magnetization	if n "easy axes" $2n$ choices	not physical
Ising model	$\langle\sigma_r\rangle$	2 choices	h
Superconductors	Δ (complex gap parameter)	phase of Δ	not physical
Superfluid	$\langle\psi\rangle$ (condensate wave function)	phase of $\langle\psi\rangle$	not physical
Ferroelectric	lattice polarization	finite number of choices	electric field
Phase separation	concentration	2 choices	a difference of chemical potentials

Generalized MFT

- *Existence* of a free energy functional $F[\varphi(r)]$
- $\varphi(\mathrm{r}) \equiv <\varphi(\mathrm{r})> + \delta\varphi(\mathrm{r})$
- *Near* critical point, can be taylor series expanded in power of $\varphi(\mathrm{r})$

$$F = \int dr \left[a - h\varphi(r) + t\varphi^2(r) + c\varphi^4(r) + \left(\nabla \varphi(r)\right)^2 \right]$$

- *Equilibrium* when F is minimized $\Rightarrow \delta F = 0$

$$-h + 2t\varphi(r) + 4c\varphi^3(r) - 2\nabla^2\varphi(r) = 0$$

What is your Broken symmetry? order parameter?

Dimension of space

Nothing New yet GREAT ADVANCE In THINKING

Summary

- Mean Field Theory
  - History: van der Waal
  - 1D Ising model
  - Correlation function Theory
  - Critical opalescence Experiment
- Landau's
  - Free energy definition
  - Why significant advance in concept?
  - An example
- Next time
  - Validity of MFT: fluctuation effect

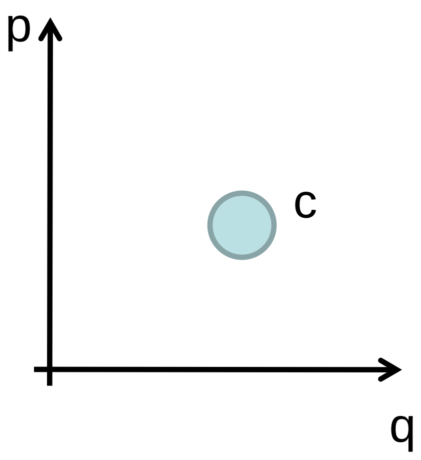
Equation Sheet

$$P = -\frac{a}{v^2} + \frac{kT}{v-b}$$

$$where\ v \equiv V / N = 1/\rho,\ a \equiv -\frac{1}{2}\int d\vec{r} V_{attr}(r),\ b \equiv v_{hardcore}$$

Classical Formulation

- $\widehat{H}(c)$
- $\beta \equiv 1/kT$
- $d\Omega \equiv dqdp$
- $p(\{q,p\} \in c)d\Omega \sim e^{-\beta(\hat{H}(c)-F)}$
- $F = -kT \ln \int d\Omega e^{-\beta \hat{H}(c)}$



Ideal Gas: PV=NkT?

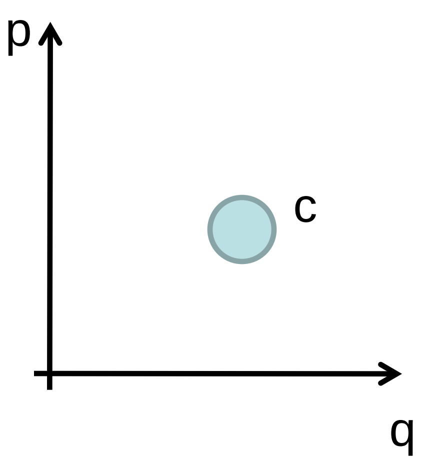
- N independent, identical particle in a box of size, V=L^3
- $\widehat{H}(c) \equiv \frac{1}{2m}\sum_{i=1}^{N} \vec{p}_i \bullet \vec{p}_i$
- $Z(\beta, N, V) = \frac{[Z(\beta,1,V)]^N}{N!}$ *where*

$$Z(\beta,1,V) = \int d^3\vec{r} \int d^3\vec{p} e^{-\beta \frac{1}{2m}\sum_{i=1}^{N} \vec{p}_i \bullet \vec{p}_i} = \frac{V}{h^3}(m2\pi kT)^{3/2}$$

- $p(\beta, N, V) \equiv -\left.\frac{\partial F(\beta, N, V)}{\partial V}\right|_{\beta,N} = \frac{N}{V}kT$

Ideal Gas: Energy Fluctuation?

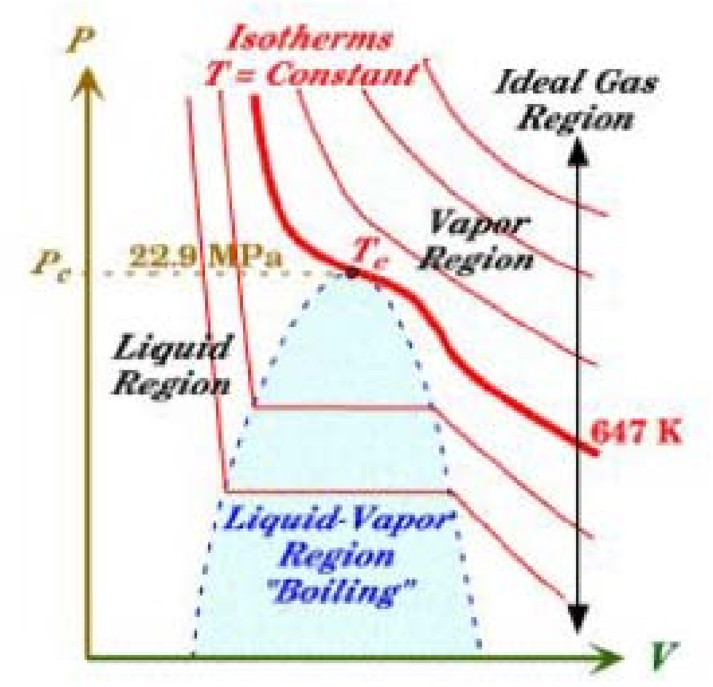
- $< H > \equiv \frac{\sum_c H e^{-\beta H[c]}}{Z} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta}\ln Z = 3N\left(\frac{kT}{2}\right)$
- *How about fluctuation in H*, $(\delta H)^2 \equiv < (H - < H >)^2 > ?$
- $< H^2 > \equiv \frac{\sum_c H^2 e^{-\beta H[c]}}{Z} = \frac{1}{Z}\frac{\partial^2}{\partial \beta^2} Z$
- $(\delta H)^2 = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} - \left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right)^2 \equiv \frac{\partial^2}{\partial^2 \beta}\ln Z(\beta, N, V)\Big|_{N,V} = \frac{1}{2}(3N)(kT)^2$
- $\frac{\delta H}{H} \sim \frac{1}{\sqrt{N}}$



1. Ideal gas, normal or Gaussian distributed in momentum

$$p(x;\mu,\sigma^2) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2}$$

Review: Water Phase Diagram



T. Andrew, “On the continuity of the gaseous and liquid states of matter,” Phil. Trans. Roy. Soc., 159, 575 (1869).

For carbon dioxide, (T,P)=(31.1^{o} C, 73 P_{at})

First MFT (of van der Waals)

$$Z(T,V,N) = \frac{1}{N!\Lambda^{3N}} \int ... \int d\vec{r}_1 ... d\vec{r}_N e^{-\beta \sum_{i<j} \phi |\vec{r}_i - \vec{r}_j|}$$

$\Lambda \equiv h / \sqrt{2\pi mkT}$ and $\phi = \phi_{attr} + \phi_{hard\ core}$

- *MFT* $\Rightarrow$ *fluctuating* field seen by the ith molecule be replaced by an average field from all others, ignoring surface effect

$$\sum_{i<j} \phi_{attr} | \vec{r}_i - \vec{r}_j | \rightarrow \sum_i \int d\vec{r}_j \phi_{attr} | \vec{r}_i - \vec{r}_j | = \sum_{i<j} 1 \left(-J \frac{N}{V} \right) = -\frac{JN^2}{2V}$$

$$Z(T,V,N) = \frac{1}{N!\Lambda^{3N}} e^{\frac{\beta JN^2}{2V}} Z_{h.c} \text{ where } Z_{h.c} = \int ... \int d\vec{r}_1 ... d\vec{r}_N e^{-\beta \sum_{i<j} \phi_{hc} |\vec{r}_i - \vec{r}_j|}$$

$$p = -\left. \frac{\partial F(T,V,N)}{\partial V} \right|_{T,N} = -\frac{JN^2}{2V^2} + p_{h.c} = -\frac{a}{v^2} + p_{h.c.}$$

- van der Waal assumes $Z_{h.c.} = (V - Nb)^N$

$$p = -\frac{a}{v^2} + \frac{kT}{v - b}$$

A cubic equation

Review

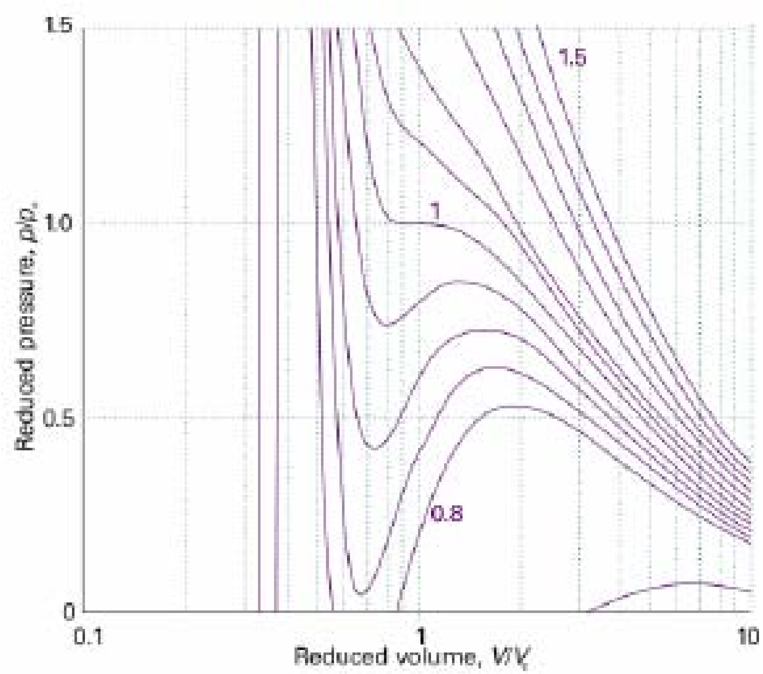


Figure 3: PVT curves predicted by the theory set up by van der Waals. The fluid is mechanically unstable whenever the pressure increases as the volume increases.

"Cubic" equation results in unstable isotherms below T_c

Appearance of a pair of complex conjugate roots.