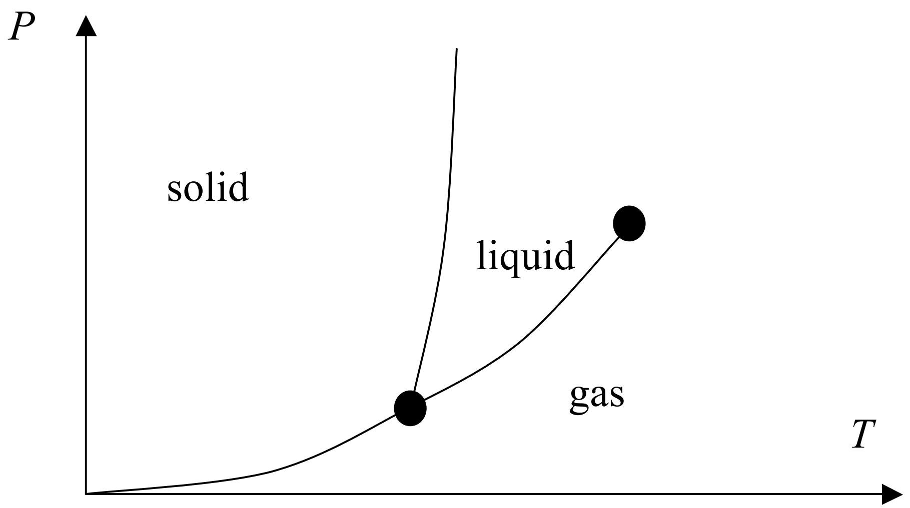
物质状态的统计物理研究

Matter: Collection of atoms/molecules

States: gas, liquid, solid (as we learned in high school)



We used to relate Structure ⇔ Mechanical Properties

But there is a lot more to it…

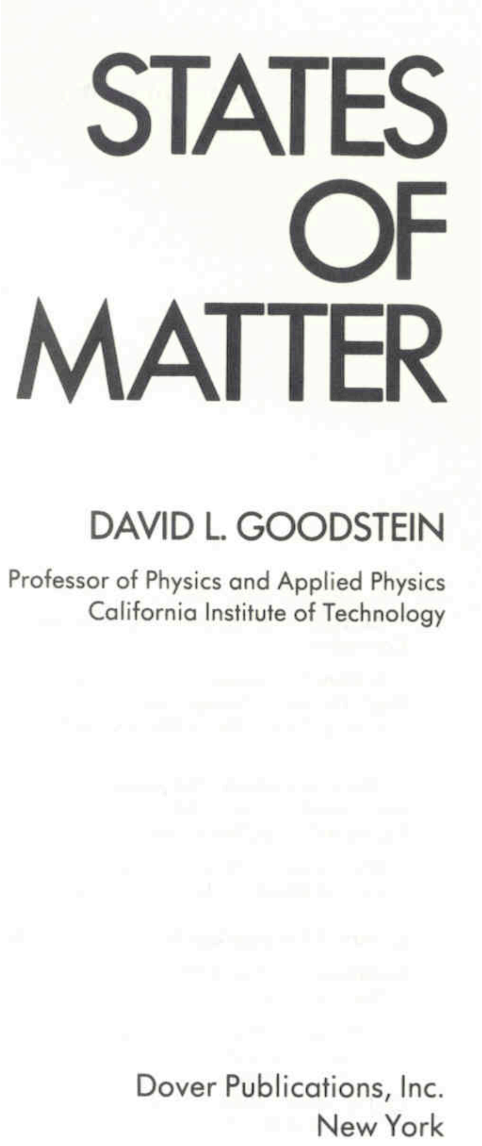
- *Electrical conduction*: metal, insulator, semiconductor, superconductor
- *Magnetism*: paramagnet, ferromagnet, etc
- *Optical*: light absorption/emission, lasing, etc.
- ……

} dynamics of electrons

and

- polymers, membranes, micelles
- DNA, RNA, proteins, molecular motors, cell, tissue, brain…

} atomic structure and dynamics



STATES
OF
MATTER

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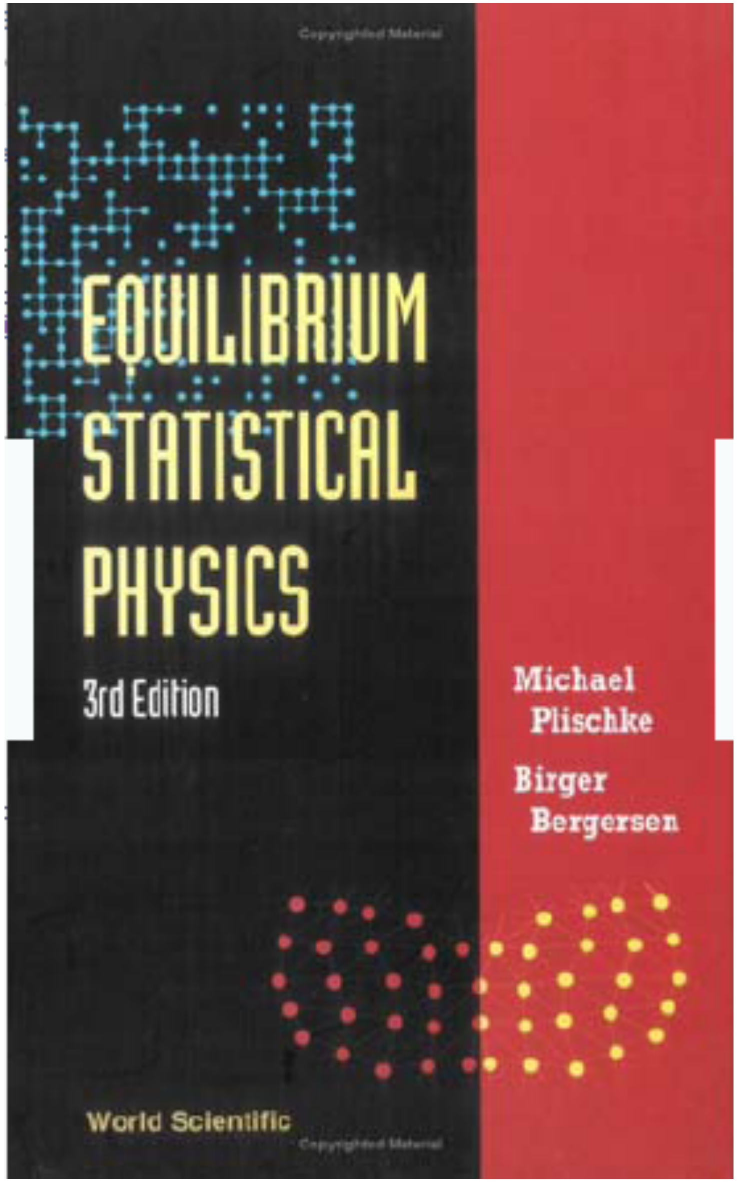
New York

Ludwig Boltzmann, who spent much of his life studying statistical mechanics, died in 1906, by his own hand. Paul Ehrenfest, carrying on the work, died similarly in 1933. Now it is our turn to study statistical mechanics.

Perhaps it will be wise to approach the subject cautiously. We will begin by considering the simplest meaningful example, the *perfect gas*, in order to get the central concepts sorted out. In Chap. 2 we will return to complete the solution of that problem, and the results will provide the foundation of much of the rest of the book.

"What we seek. ..is a feeling for the essential nature of the stuff, and how one goes about studying it."

-PROFESSOR GOODSTEIN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中文译本年底出版？

A brief history of condensed matter and statistical physics

1930's: development of band theory of solids soon after QM was established. Electronic origin of magnetism was also proposed and studied; The Fermi liquid theory; Landau theory of phase transitions

1940's: invention of semiconductor devices that changed the world; Onsager's exact solution of the Ising model

1950's: theory of superconductivity was established; Feynman's theory of superfluidity.

1960's: many-body theory of electronic states and various field theoretic methods were developed. Off-diagonal long-ranged order; Scaling theory of phase transitions

1970's: renormalization group theory applied to phase transitions and critical phenomena. Deeper view of ordered states and their stability.

1980's: study of glassy systems. New understanding of nonequilibrium systems and their dynamics. The quantum Hall effect. High-Tc superconductivity rekindled interest in electronic systems with strong correlation

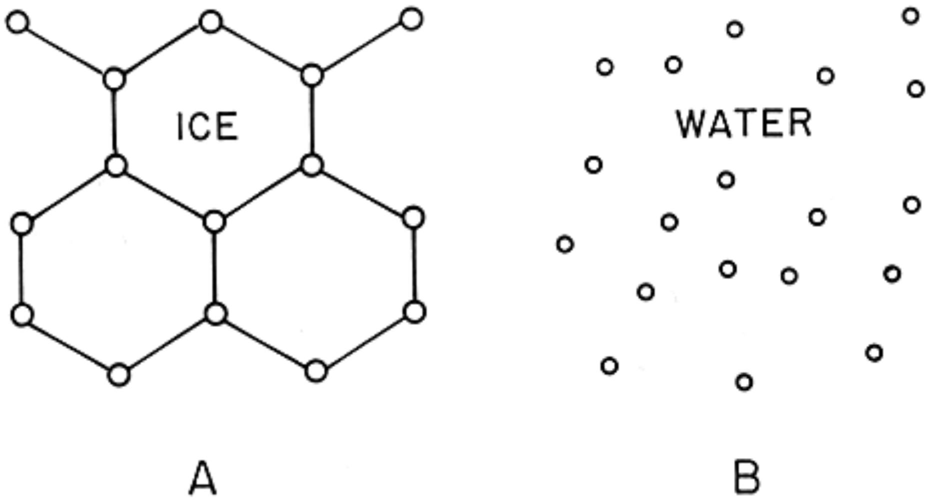
1990's: nano-technologies and devices, improvements in computational techniques and capabilities.

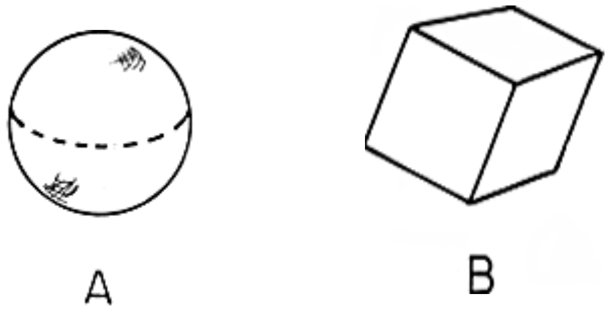
2000's: complex networks and biological systems…

Classification of states of matter by their symmetry

(Jim Sethna: Classification of Phases)

Atoms/molecules can organize in many different forms

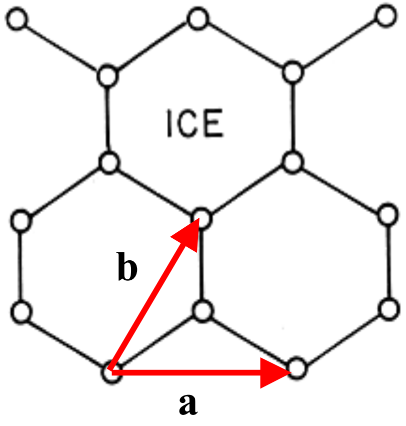




Which one is more symmetric?

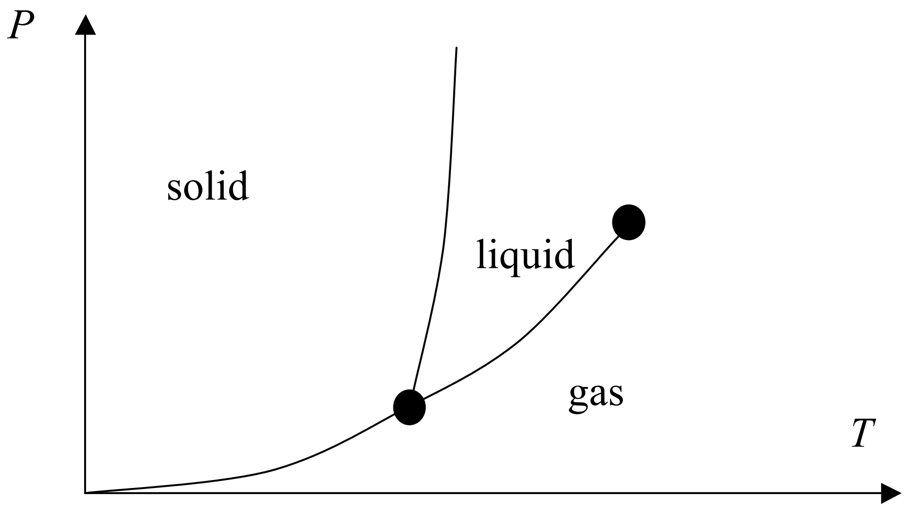
Liquid is more symmetric than crystal because we can rotate it (or we rotate ourselves) in any way and won't notice a difference.

For a single crystal, the basis vectors of the crystal lattice specifies the orientation of the atomic/molecular bonds and their spatial positions of the atoms. Even though we did not pick any special direction for the bonds nor special positions for the atoms, the molecules themselves organize into a structure that breaks both translational and rotational symmetry of space.



Hence we could say the liquid and solid phases are separated by a symmetry change.

Symmetry is a more fundamental concept than other properties as it is either there or not there. It can be used unambiguously to define the transition between different phases of matter. On the other hand, not all phase transitions are accompanied by a symmetry change.



Questions of more quantitative nature

Questions:

- Why do the water molecules form ice below T=273.16?
- Why do they form the particular crystal structure?
- How can one characterize the atomic structure of an ice crystal?
- What are the consequences of symmetry breaking?

Answers:

- We need to know how water molecules interact with each other. (E&M and QM)
- We need to use methods of Statistical Mechanics to find the state with the least free energy at a given temperature and pressure
- We need to define an order parameter
- We need to develop a general theory of deformations from a perfectly ordered structure (in this case phonons)

相变的热力学

Gibbs free energy and chemical potential

The Gibbs free energy is defined as

$$\Phi(T,P,N) = E - TS + PV \qquad (1.2.12)$$

Eq. (1.1.20) yields,

$$d\Phi = -SdT + VdP + \mu dN \qquad (1.2.28)$$

Since both *P* and *T* are intensive variables, we have

$$\Phi = \mu N \qquad (1.2.36)$$

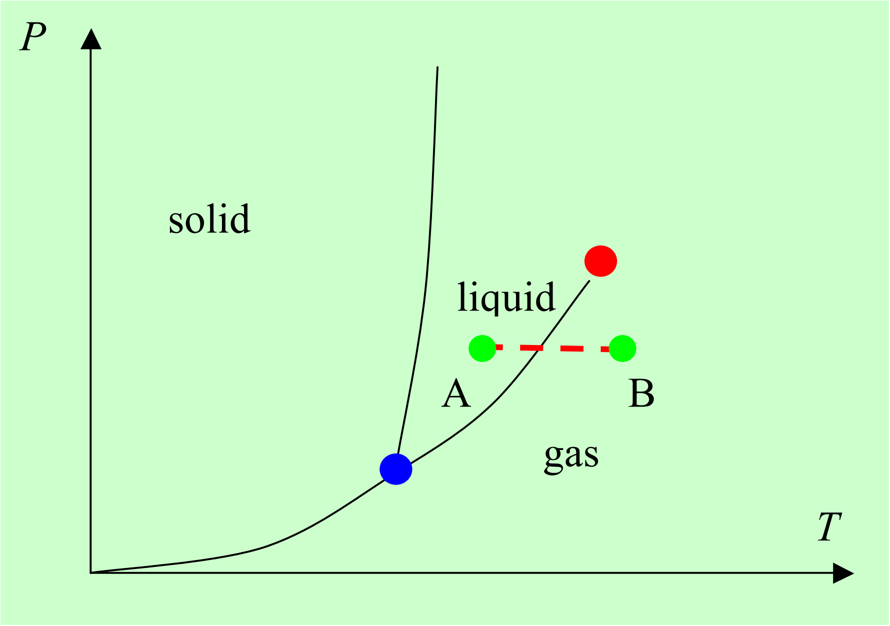
When two phases coexist, we may move particles from one phase into the other without changing the total Gibbs free energy. Therefore a condition for phase coexistence is

$$\mu_1(P,T) = \mu_2(P,T) \qquad (1.2.123)$$

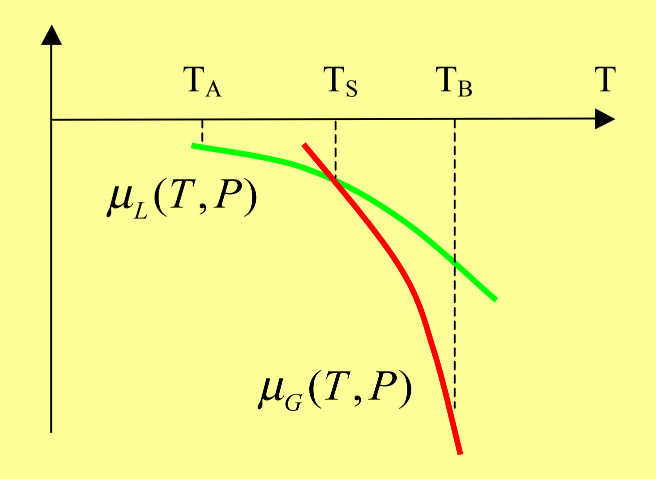
Since there is only one equation but both P and T can vary, two phase coexistence in a single component system can take place along a line. On the other hand, for three phase coexistence, we have two equations and two unknowns. Hence it happens only at a point on the P-T diagram (the triple point).

Example: Liquid-gas transition

At Point A on the P-T diagram, the particle system is in the liquid state. As one increases temperature at a constant pressure (i.e. heating up the system), the system initially stays in liquid form, but changes into gas form when one reaches the **coexistence line**.



The thermodynamics of the phase change can be carried out by examining the behavior of the chemical potential in the two phases, $\mu_L(T,P)$ and $\mu_G(T,P)$, respectively. At a given P and T, the phase with lower chemical potential is the equilibrium phase. Note that μ as a function of T is continuous at the transition but its slope isn't!



Change of various quantities across a phase boundary:

Gibbs free energy Φ: continuous

First order derivatives

$S = -\partial\Phi/\partial T\big|_P$: jumps at the transition

$V = -\partial\Phi/\partial P\big|_T$: jumps at the transition (density)

$E = \Phi + TS - PV$: jumps at the transition

Second order derivatives

$C_P = -T\partial^2\Phi/\partial T^2\big|_P$: infinite

$\kappa_T = -\frac{1}{V}\partial^2\Phi/\partial P^2\Big|_T$: infinite

At the critical point:

S, V, E continuous, but specific heat and isothermal compressibility diverge.

In general, phase transition point can be identified with the mathematical singularity of the free energy function.

格点伊辛模型

The Ising model

i) Hamiltonian: $$\boxed{H(\{\sigma_i\}) = -J\sum_{\langle ij\rangle}\sigma_i\sigma_j - h\sum_i \sigma_i}$$

The spin variables $\sigma_i = \pm 1$ are assigned to sites on a *d*-dimensional lattice.

—The simplest model to explain development of spontaneous magnetization of a magnetic system at low temperatures. (phase diagram?)

—Related to gas-liquid transition, phase separation in binary alloys etc.

ii) Observations

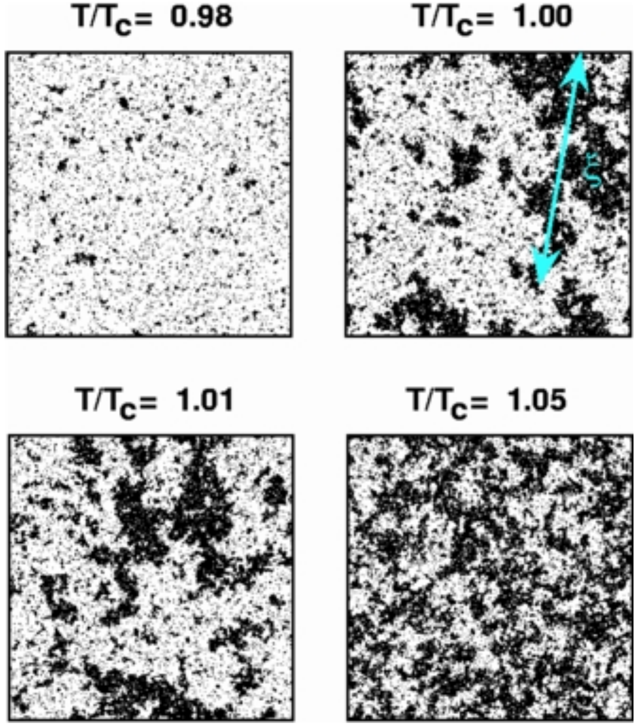
Ground state at *h* = 0 (ferromagnetic coupling, *J* > 0):

$\sigma_i = 1$, all i,

or $\sigma_i = -1$, all i.

Either state breaks the symmetry $\sigma \to -\sigma$ of the Hamiltonian

At finite temperature: $\boxed{F = E - TS}$ should be minimized



At sufficiently low temperatures, due to the energetic preference, the system goes to a symmetry-breaking state. (Majority/minority)

Symmetry is restored in the paramagnetic phase at high temperatures. (homogeneous)

The ordering process is gradual and continuous. Large scale fluctuations at the transition point.

The symmetry-breaking state is more ordered than the symmetric one. Thus the phase transition corresponds to the onset of order in the system, which can be described quantitatively with an **order parameter**: $m = \frac{1}{N}\sum_i \sigma_i$.

iii) Why is it a hard problem?

$$Z_N(T,h)=\sum_{\{\sigma_i=\pm1\}}\exp\left[-\beta H\left(\{\sigma_i\}\right)\right]$$

2^N terms in the sum, to express the result in closed form function of *T* and *h* seems to be quite nontrivial.

A case we know how to treat (stat phys I): noninteracting spins in a field (*J* = 0)

$$Z_N(T,h)=z^N(T,h)$$

$$z(T,h)=\sum_{\sigma=\pm1}e^{\beta h\sigma}=e^{\beta h}+e^{-\beta h}=2\cosh\left(\beta h\right)$$

Key to success: factorization! i.e., separate the degrees of freedom into independent ones, each involving a small number of terms.

—In this case, the scheme of separation is obvious.

—In the more general case, perhaps there are ways of doing it if we prepare (massage) the problem sufficiently.

Such “divide-and-conquer” tactic is used everyday in research!

Back to the Ising model:

- Use the noninteracting case as the reference point: high temperature series expansion
- Representing the effect of neighbors by a “mean-field”, close the equation with a self-consistent condition
- Use a factorized form to approximate the true Boltzmann distribution, and determine the parameters based on variational principle (Bragg-Williams, Bogoliubov inequality)
- Transfer matrix: generalization of the factorization to matrix products
- Coarse-graining: focus on degrees of freedom that represent local averages, and construct effective Hamiltonians for the “slow variables”. This is the basis for the Ginzburg-Landau theory and the renormalization group approaches.

iv) Bragg-Williams approximation formulated from a variational point of view.

"Trial Hamiltonian": $H_0 = -\tilde{h}\sum_i \sigma_i$ $\tilde{h}$ is the variational parameter

$$p_\pm = \frac{e^{\pm\beta\tilde{h}}}{e^{\beta\tilde{h}} + e^{-\beta\tilde{h}}}, \qquad m = p_+ - p_- = \tanh\left(\beta\tilde{h}\right), \quad \beta\tilde{h} = \frac{1}{2}\ln\frac{p_+}{p_-} = \frac{1}{2}\ln\frac{1+m}{1-m}$$

$$F_0 = -Nk_BT\ln\left[2\cosh\left(\beta\tilde{h}\right)\right] = -Nk_BT\ln 2 + \frac{1}{2}Nk_BT\ln(1-m^2)$$

$$\left\langle H_0\right\rangle_0 = -N\tilde{h}m = -\frac{1}{2}Nk_BTm\ln\frac{1+m}{1-m}, \quad \left\langle H\right\rangle_0 = -J\frac{Nq}{2}m^2 - Nhm$$

$$\boxed{\begin{aligned} F_{\text{var}}(m) &= F_0 + \left\langle H\right\rangle_0 - \left\langle H_0\right\rangle_0 \\ &= -J\frac{Nq}{2}m^2 - Nhm + Nk_BT\left[\frac{1+m}{2}\ln\frac{1+m}{2} + \frac{1-m}{2}\ln\frac{1-m}{2}\right] \end{aligned}}$$

Minimizing w.r.t. *m* (equivalent to minimizing w.r.t. $\tilde{h}$) yields

$$\boxed{m = \tanh\left[\beta\left(qJm + h\right)\right]}$$

v) Nature of the solution and possible improvements

Consider the above approximation at h=0

— at *T* = 0, $m=\pm 1$, $F=-NqJ/2$ okey, dominant nearest neighbor interaction is taken care of.

— at $T=\infty$, $m=0$, $F=-Nk_BT\ln 2$, also okey.

— However, the self-consistent equation yields $m=0$ and hence $E=0$ for any $T>T_c$. This is not quite right. Reason: energetic preference for neighbors to align completely ignored in the high temperature phase.

— The above can be corrected by allowing for some correlation between nearest neighbors with an improved variational Hamiltonian. But the calculation will become much more involved.

— This way of improvement will probably never work sufficiently close to T_c.

Success: Since the calculation correctly reproduces the system behavior at zero and infinite temperatures, the spontaneous ordering phenomenon is captured. In addition, various thermodynamic quantities show singular behavior at the transition.

Failure: Details of the ordering transition is not only incorrect at the quantitative level, it is incorrect at a qualitative level below four dimensions (as compared to experiments and computation). The origin of this failure lies in its inability to capture correlations on increasing larger scales as the critical point is approached. Such large scale correlations give rise to the singular behavior of various thermodynamic quantities.

vi) Properties of the solution (left as an exercise)

vii) Lessons learned

- A calculation that captures the limiting behavior can be used to learn more about the system, as a first step.
- Analytic solution/handle, even approximate ones, allows one to sketch an overall picture of the system's behavior as a function of the controlling parameters, in this case temperature and external field. Various limiting properties and dependencies can be discussed, as well as how different quantities are related to each other, etc., even though important details are not all described accurately.
- The simplicity of the approximate solution, if done correctly, can be more useful in exposing the physics involved.
- Once the weaknesses of a particular approximation is understood, one can proceed to
- construct more refined theory targeted at the unsolved aspects of the problem.

In this sense we can now move on to the more sophisticated treatments: coarse-grained continuum description as in the Ginzburg-Landau theory and the renormalization group treatment.

临界现象的标度律及临界指数

Widom scaling – Kadanoff’s block spins – Ken Wilson’s renormalization group

ME Fisher, Rev Mod Phys **70**, 653-681 (1998)

Critical Point Exponents

Summary of various “singular behavior” at the critical point:

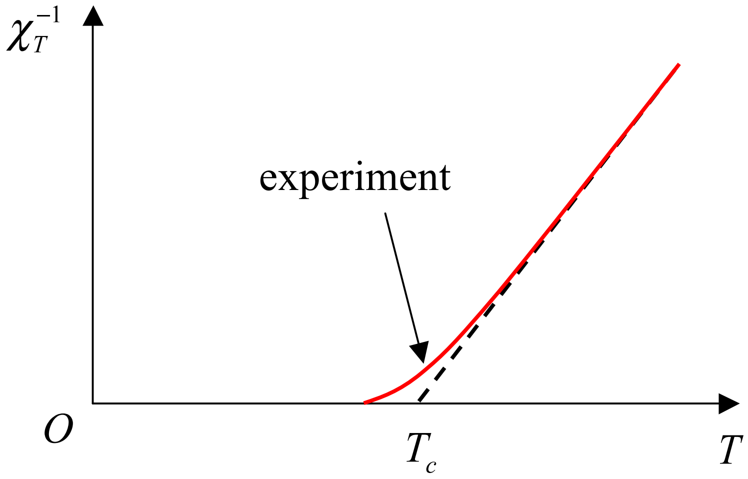
- order parameter vanishes
- magnetic susceptibility/compressibility diverges
- heat capacity jumps/diverges
- correlation length diverges
- …

The mean-field theories give specific predictions on how these quantities go to zero or infinity as $T \to T_c$, but these often do not agree with experiments.

Example: magnetic susceptibility

Mean-field: $\chi_T \sim (T - T_c)^{-1}$

Better described by $\chi_T \sim \left(T - T_c\right)^{-\gamma}$, with $\gamma = 1.1$ to 1.4.



Definition of critical exponent:

If a function $f(t)$ diverges or goes to zero as $t \equiv \frac{T - T_c}{T_c} \to 0$, one may define a critical exponent (assuming the limit exists)

$$\lambda \equiv \lim_{t \to 0} \frac{\ln f(t)}{\ln t}$$

and write, in the neighborhood of the critical point, $f(t) \sim t^{\lambda}$.

In general, the function $f(t) = At^{\lambda} + Bt^{\lambda_1} + \ldots$ ($\lambda_1 > \lambda$) may contain corrections to the leading-order term. This may generate a lot of headache in experimental or numerical determination of the critical exponents.

Most commonly used critical exponents

Specific heat: $C \sim t^{-\alpha}$

Order parameter: $m \sim (-t)^{\beta}$

Susceptibility/compressibility: $\chi \sim t^{-\gamma}$

Critical isotherm ($t = 0$): $h \sim m^{\delta}$

Correlation length: $\xi \sim |t|^{-\nu}$

Pair correlation function ($t = 0$): $c(r) \sim r^{-(d-2+\eta)}$

Scaling laws (critical exponent identities)

$$\boxed{\begin{aligned} &\alpha + 2\beta + \gamma = 2, \quad d\nu = 2 - \alpha \\ &\beta(\delta - 1) = \gamma, \quad \gamma = (2-\eta)\nu \end{aligned}}$$

But where do they come from?

Scaling hypothesis

Free energy per site: $g(t,h)=g_0(t,h)+g_s(t,h)$

At $h=0$, $g_s(t,0)\sim|t|^{2-\alpha}$

"Scaling": $t\to bt,\;\; g_s\to b^{2-\alpha}g_s$

At $t=0$, $g_s(0,h)\sim h^{1+1/\delta}$

"Scaling": $h\to bh,\;\; g_s\to b^{1+1/\delta}g_s$

Homogeneity hypothesis (Ben Widom, 1965): $\boxed{g_s(t,h)=\lambda^{-d}g_s(\lambda^y t,\lambda^x h)}$

(x,y take values that are model specific)

With this assumption, we obtain,

$$\boxed{\begin{aligned} m(t,h)&=-\frac{\partial g}{\partial h}=\lambda^{-d+x}m(\lambda^y t,\lambda^x h)\\ c_h(t,h)&=-T_c^{-1}\frac{\partial^2 g}{\partial t^2}=\lambda^{-d+2y}c_h(\lambda^y t,\lambda^x h)\\ \chi(t,h)&=-\frac{\partial^2 g}{\partial h^2}=\lambda^{-d+2x}\chi(\lambda^y t,\lambda^x h)\end{aligned}}$$

Special cases:

i) $h=0, \lambda = |t|^{-1/y}$;

$$\boxed{\begin{aligned} m(t,0) &= (-t)^{(d-x)/y}\, m(-1,0) \\ c_h(t,0) &= |t|^{(d/y)-2}\, c_h(\pm 1,0) \\ \chi(t,0) &= |t|^{-(2x-d)/y}\, \chi(\pm,0) \end{aligned}}$$

ii) $t=0, \lambda = |h|^{-1/x}$

$$\boxed{m(0,h) = |h|^{(d/x)-1}\, m(0,\pm 1)}$$

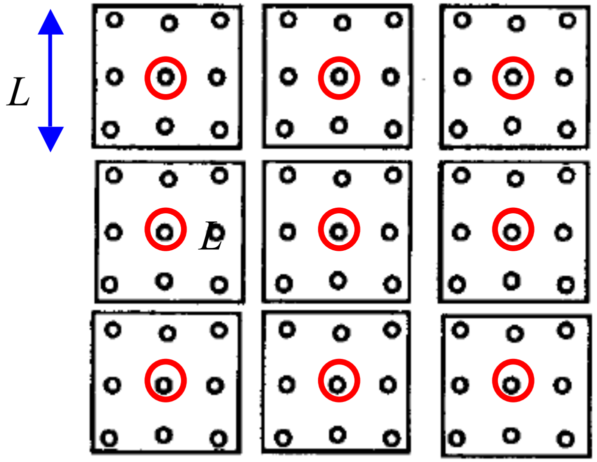
Hence,

$$\boxed{\begin{aligned} \alpha &= 2-(d/y) \\ \beta &= (d-x)/y \\ \gamma &= (2x-d)/y \\ \delta &= x/(d-x) \end{aligned}}$$

$$\boxed{\begin{aligned} \alpha+2\beta+\gamma &= 2 \\ \beta(\delta-1) &= \gamma \end{aligned}}$$

But why?

Kadanoff block spins



For a historical account, read pages 10-18 of Leo Kadanoff's article *From Order to Chaos II*.

Block spin transformation (coarse-graining): $\sigma_i \to \tilde{\sigma}_J = \mathrm{sign}\left(\sum_{i\in J}\sigma_i\right)$

known as the *majority rule*

i) The original and transformed system share the same critical point $\Rightarrow$ At this special point, the system becomes scale invariant!

ii) Away from the critical point, $\boxed{t \to \tilde{t} = tL^y, \quad h \to \tilde{h} = hL^x}$ (key assumption)

iii) Free energy per site: $g_s \to \tilde{g}_s = g_s(\tilde{t},\tilde{h}) = L^d g_s(t,h)$, or $\boxed{g_s(t,h) = L^{-d} g_s(L^y t, L^x h)}$!

In addition, Kadanoff's scaling analysis yields a prediction of the spatial structure of critical fluctuations.

Scale of physical quantities in the critical region

Correlation length: ξ

(Free) Energy: kT_c

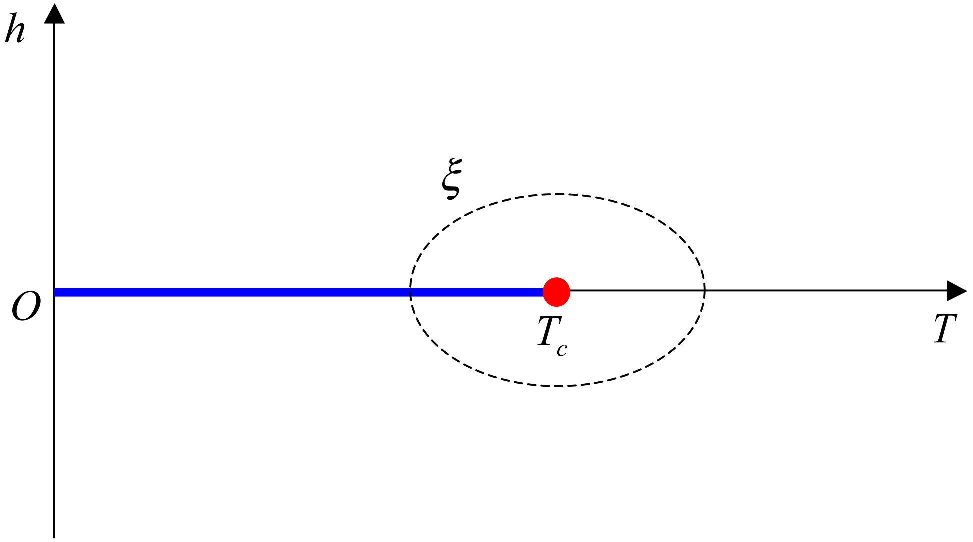
Upon the block transformation, $\xi(t,h) \to \tilde{\xi} = \xi(\tilde{t},\tilde{h}) = \xi(t,h)/L$

Hence: $\boxed{\xi(t,h) = L\xi(L^y t, L^x h)}$

Divergence of ξ

$h=0$: $\xi \sim |t|^{-\nu}$, $\nu = 1/y$

$T=T_c$: $\xi \sim |h|^{-1/x}$



Hyperscaling relation: $\boxed{\alpha = 2 - d/y = 2 - d\nu}$

Evaluation and summary: testing the scaling laws

1. Critical point exponents are difficult to measure experimentally.
2. Experimental physicists have worked extremely hard to achieve the unachievable, and along the way improved their instruments as well as our understanding of Nature.
3. The scientific process of verifying a hypothesis is often biased despite the presumed honesty and integrity shown by most scientists in their investigations.
4. The scaling theory has been a tremendeous success when compared with experimental data. It is now part of the “established wisdom” of the scientific community. It has been applied to many different areas of science in addition to the equilibrium critical phenomena where the ideas were first developed.

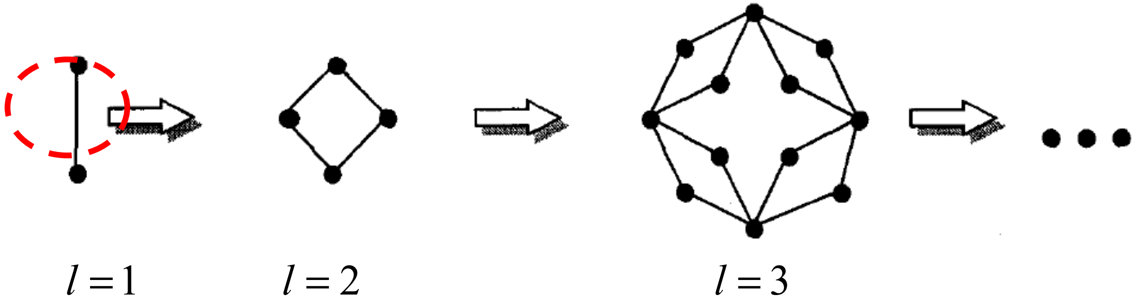
5. Beyond the scaling theory, the renormalization group ideas were developed and implemented. The mean-field theories were shown to give a correct description above four dimensions, but fluctuations “renormalize” parameters in the Landau free energy functional as one goes to larger and larger scales, yielding different set of values for the exponents.

6. With the availability of powerful computers, predictions of the scaling theory have been verified to great precision for many different types of phase transitions, and universality classes have been identified.

7. We have witnessed a beautiful example of scientific research in modern history. From van der Waals to Ken Wilson, it took a century for the correct ideas to be developed and subtleties of Nature understood.

Ising Spins on the Diamond Fractal Lattice (Migdal-Kadanoff real-space RG)

Lattice generated through an iterative procedure



Placing Ising spins on the vertices of the lattice.

Summation of spins on the middle vertices of a diamond renormalizes the interaction and field strength on the upper and lower vertices:

$$Z(N,J,H)=e^{Ng(J,h)}Z(N/4,J',h')$$

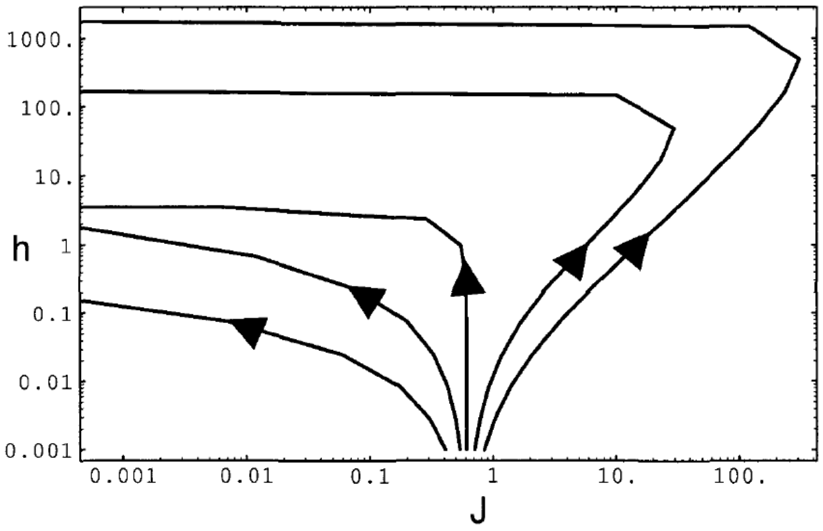
Same as the 1D Ising chain except each time two branches contribute, so the results differ by a factor of 2.

$$g=\frac{1}{8}\ln[16\cosh(2J+h)\cosh(2J-h)\cosh^2 h]$$

$$J'=\frac{1}{2}\ln\left[\frac{\cosh(2J+h)\cosh(2J-h)}{\cosh^2 h}\right]\equiv R_1(J,h)$$

$$h'=h+\ln\frac{\cosh(2J+h)}{\cosh(2J-h)}\equiv R_2(J,h)\ .$$

Renormalization Group flow



Critical point at

$h^* = 0$

$J^* = 0.60938$

singular part of the free energy must thus be of the scaling form

$$f_s(t,h) = \frac{1}{4} f_s\left(\frac{\partial R_1}{\partial J} t, \frac{\partial R_2}{\partial h} h\right) = \frac{1}{\lambda} f_s(\lambda^y t, \lambda^x h)$$

with $\lambda = 4$ and

$$y = \frac{\ln 1.67857}{\ln 4} = 0.373618$$

$$x = \frac{\ln 2.67857}{\ln 4} = 0.710732$$

from which we find the critical exponents

$$\alpha = \frac{2y-1}{y} = -0.676532$$

$$\beta = \frac{1-x}{y} = 0.774234$$

$$\gamma = \frac{2x-1}{y} = 1.12806$$

$$\delta = \frac{x}{1-x} = 2.45701 \quad .$$

Cusp singularity for the specific heat (with a negative α)