15. Statistical mechanics of magnetic systems

non-interacting magnets

N interacting magnets

Ising model

STATISTICAL MECHANICS OF NON-INTERACTING MAGNETS

Microcanonical treatment:

Consider a set of N non-interacting atoms in the gas phase.

The energy for any one atom is

$$\epsilon = \epsilon_{transl} + \epsilon_{elec}$$

The molecular partition function is

$$q = q_{transl} \cdot q_{elec} \qquad u = -kT \ln \frac{q}{N}$$

The Gibbs free energy is Nu

$$G = -NkT \ln \frac{q}{N}$$

$$= -NkT \ln \frac{q_{tr}}{N} - NkT \ln q_{elec}$$

The electronic contribution to the energy is

$$E_{elec} = NkT^2 \frac{\partial (\ln q_{elec})}{\partial T}$$

First consider the case where all excited states have energies very large compared to kT and only the lowest electronic state is important. This ground state is given by ${}^{2S+1}L_J$. The values of m_J are $\underbrace{-J, -J+1, \cdots +J}_{2J+1 \text{ of these}}$

$$\therefore q_{elec} = (2J+1)e^{\epsilon_0/kT} + \cdots \simeq 2J+1$$ neglecting excited electronic states

For N non-interacting magnets in a lattice

$$Q = q_{elec}^N$$

Now turn on a magnetic field B. The energy levels are

μ_B = Bohr magneton

g = Lande g factor for that electronic state

— $+3/2$

— $+1/2$

— $-1/2$

— $m = -3/2$ $\quad \epsilon_m = g\mu_B m B$

$$\mu^2 = g^2 \mu_B^2 J(J+1)$$

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

= a constant for a given electronic state $^{2S+1}L_J$

In the presence of the field the electronic partition function is

$$q_{elec}(B,T) = \sum_{m=-J}^{m=+J} e^{-g\mu_B m B/kT}$$

Let $y = g\mu_B B/kT$ $\qquad q_{elec}(B,T) = \sum_{m=-J}^{+J} e^{-my}$

The probability of observing an atom in the state m is

$$\frac{N_m}{N} = \frac{e^{-\epsilon_m/kT}}{q} = \frac{e^{-my}}{q}$$

The average magnetic moment per particle is

$$\langle \mu_z \rangle = \frac{\sum_m (-g\mu_B m)\, e^{-my}}{q} \qquad \text{since } \langle \mu_z \rangle_m = -g\mu_B m$$

$$= \frac{kT}{q}\left(\frac{\partial q}{\partial B}\right)_T \quad \text{or} \quad \frac{\langle \mu_z \rangle}{g\mu_B} = \frac{1}{q}\frac{dq}{dy}$$

$M = N\langle \mu_z \rangle$

$\chi_m = \frac{M}{B}$

$$\langle \epsilon \rangle = \frac{\sum_m (g\mu_B m B) e^{-my}}{q} = -\langle \mu_z \rangle B$$

$$E = N\langle \epsilon \rangle$$

Except at very low temperatures and very large fields, $y \ll 1$, therefore,

$$e^{-my} \approx 1 + my + \frac{m^2 y^2}{2} + \cdots \quad \text{"high temperature" limit}$$

Note also that

$$\sum_{m=-J}^{+J} m = 0$$

$$\sum_{m=-J}^{+J} m^2 = \frac{J(J+1)(2J+1)}{3}$$

Now, at this "high temperature" limit,

$$q_{\text{free}}(B,T) = \sum_{m=-J}^{+J} e^{-my} \Longrightarrow$$

$$\sum_{m=-J}^{+J} 1 + y\sum_{m=-J}^{+J} m + \frac{y^2}{2}\sum_{m=-J}^{+J} m^2$$

$$= 2J+1 + 0 + \frac{y^2}{6} J(J+1)(2J+1)$$

$$= (2J+1)\left[1 + \frac{J(J+1)y^2}{6}\right]$$

$$= (2J+1)\left[1 + \frac{J(J+1) g^2 \mu_B^2 B^2}{6k^2T^2}\right]$$

$$= (2J+1)\left[1 + \frac{\langle \mu^2 \rangle B^2}{6k^2T^2}\right]$$

$$\frac{\langle \mu_z \rangle}{g\mu_B} = \frac{-1}{g}\frac{dg}{dy} \approx \frac{J(J+1)}{6}\,2y \qquad \langle \mu^2 \rangle$$

$$\therefore \quad \langle \mu_z \rangle \approx \frac{g^2 \mu_B^2 J(J+1)}{3kT} B$$

$$\langle \mu_z \rangle \approx \frac{\langle \mu^2 \rangle B}{3kT}$$

$$\boxed{\chi_M} = N_{Avo}\frac{\langle \mu_z \rangle}{B} = \boxed{N_{Avo}\frac{\langle \mu^2 \rangle}{3kT}} - N_{Avo}\,\chi_{diam}^{(atom)}$$

diamagnetic susceptibility of an atom

from $M = N\langle \mu_z \rangle = \chi_M B$

$$\therefore \quad M = N_{Avo}\left[\chi_{diam}^{(atom)} + \frac{\langle \mu^2 \rangle}{3kT}\right] B$$

This is analogous to

$$P = N_{Avo}\left[\alpha + \frac{\mu^2}{3kT}\right) F = \frac{\epsilon - 1}{4\pi} F$$

electric polarization

α = electric dipole polarizability

μ = electric dipole moment

ϵ = dielectric coefficient

which can be derived in the analogous way, except that electric moments are treated as classical, i.e., can take any orientation in the electric field F.

The thermodynamic properties will have magnetic contributions:

$$E = -N\langle \mu_z \rangle B = -N\frac{\langle \mu^2 \rangle B^2}{3kT}$$

$$\ln(1+x) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3 - \cdots$$

$$A = -NkT \ln g = -NkT \ln(2J+1) - NkT \ln\left(1 + \frac{\langle \mu^2 \rangle B^2}{6k^2T^2}\right)$$

$$\approx -NkT \ln(2J+1) - \frac{g^2\mu_B^2 B^2 J(J+1)}{6k^2T^2} NkT$$

$$S = \frac{E-A}{T} = Nk \ln(2J+1) - \frac{g^2\mu_B^2 B^2 J(J+1)}{6k^2T^2} Nk$$

Let us go back to the entropy of the spin system in B_0

$$S = \underbrace{Nk \ln(2J+1)}_{\text{spins}} - \frac{g^2 \mu_B^2 B_0^2}{6k^2T^2} J(J+1) Nk_{\text{spins}} + S_{\text{lattice}}$$

residual entropy due to random orientation of spins

N_{spins} could be only a fraction of N (dilute in the paramagnetic ions)

should go to zero as spin system becomes ordered

EVEN IN THE ABSENCE OF A MAGNETIC FIELD

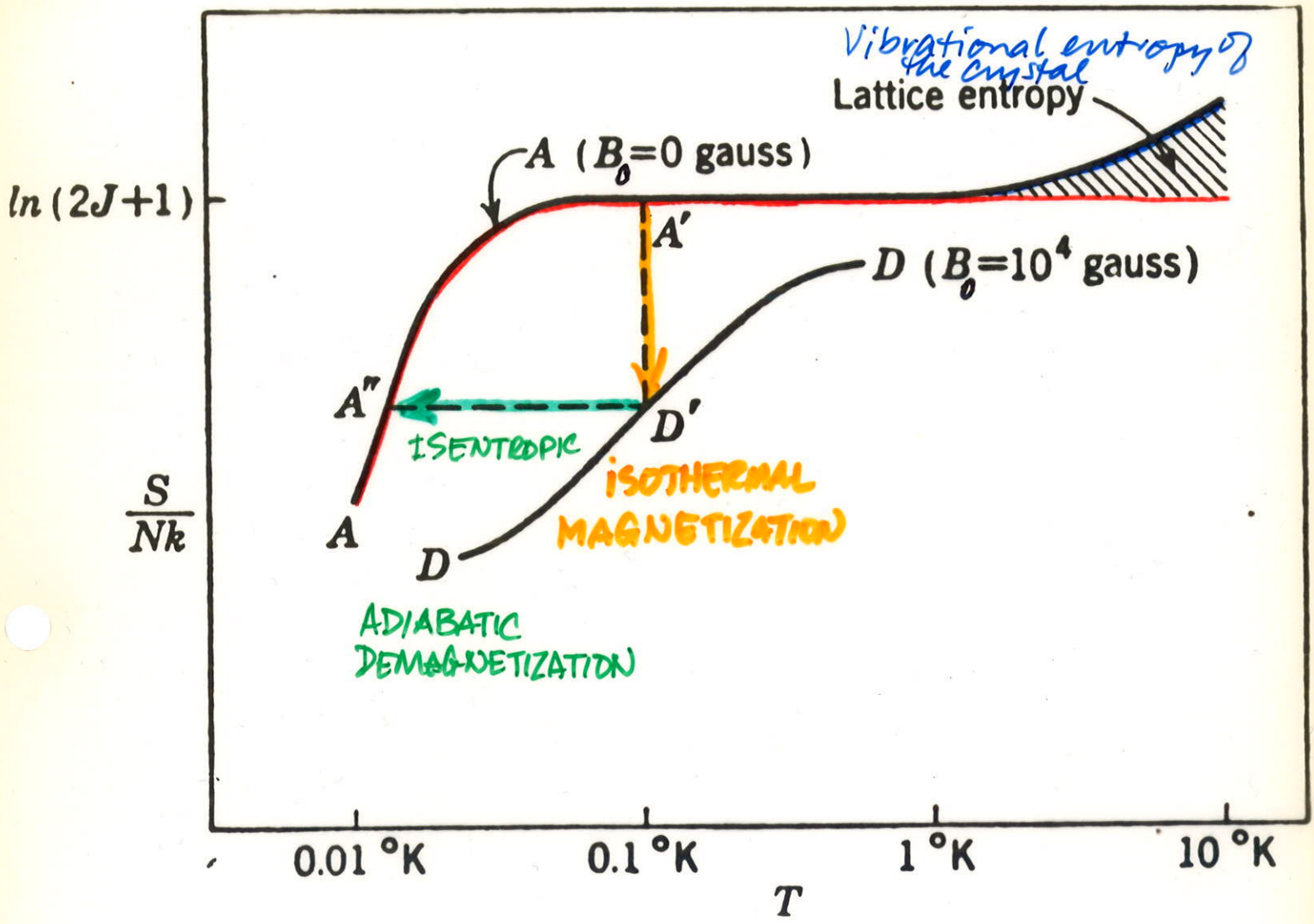
vibrational entropy of the crystal

From Debye theory at low temperatures

$$S_{\text{lattice}} \approx Nk \frac{4\pi^4}{5} \left(\frac{T}{\theta_D}\right)^3$$

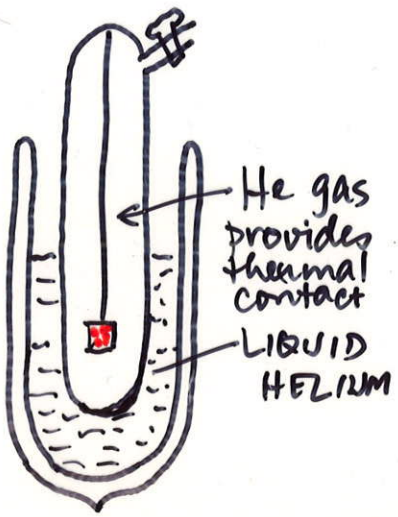
In the presence of the magnetic field the spins line up with the magnetic field, decreasing S, more pronounced effect as T decreases since $S \sim -\frac{a B_0^2}{T^2}$

Entropy-temperature diagram



EVACUATE the He to remove thermal contact, then decrease B_0

paramagnetic salt



APPLY A MAGNETIC FIELD B_0

released heat boils off liquid Helium

N INTERACTING MAGNETS

For a system of N particles of spin J there are $(2J+1)^N$ system quantum states
The energy of the jth system quantum state is $E_j(B_0)$
The magnetic moment of the system in the jth system quantum state is defined as

$$M_j \equiv -\frac{dE_j(B_0)}{dB_0}$$

Canonical partition function =

$$Q(B_0,T) = \sum_j e^{-E_j(B_0)/kT}$$

Probability of finding a system in state j is

$$P_j = \frac{n_j}{n} = \frac{e^{-E_j(B_0)/kT}}{Q(B_0,T)}$$

Ensemble average of M, the magnetic moment of the system,

$$\bar{M}(B_0,T) = \sum_j P_j M_j = \frac{1}{Q(B_0,T)} \sum_j \frac{-dE_j(B_0)}{dB_0} e^{-E_j(B_0)/kT}$$

$$= kT\left(\frac{\partial \ln Q(B_0,T)}{\partial B_0}\right)_T$$

The ensemble average of E is

$$\bar{E}(B_0,T) = \frac{1}{Q}\sum_j E_j e^{-E_j(B_0)/kT} = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{B_0}$$

The fundamental eqn of canonical ens.

$$A = -kT \ln Q \quad \text{explicitly: } A(B_0,T) = -kT \ln Q(B_0,T)$$

Entropy is

$$S(B_0,T) = \frac{E-A}{T} = kT\left(\frac{\partial \ln Q}{\partial T}\right)_{B_0} + k \ln Q$$

$$= -\left[\frac{\partial A(B_0,T)}{\partial T}\right]_{B_0}$$

Ensemble average of M can be written as:

$$\bar{M}(B_0,T) = kT\left(\frac{\partial \ln Q(B_0,T)}{\partial B_0}\right)_T = \left(\frac{\partial\, kT \ln Q}{\partial B_0}\right)_T = -\left[\frac{\partial A}{\partial B_0}\right]_T$$

From the above relations we found that

$$S = -\left[\partial A/\partial T\right]_{B_0} \qquad \bar{M} = -\left[\partial A/\partial B_0\right]_T$$

Let us use $\dfrac{\partial^2 A}{\partial T \partial B_0} = \dfrac{\partial^2 A}{\partial B_0 \partial T}$ since dA is an exact differential

$$\therefore \left(\frac{\partial S}{\partial B_0}\right)_T = \left(\frac{\partial \bar{M}}{\partial T}\right)_{B_0}$$

NEGATIVE. (Curie law) — used in magnetic cooling

For N particles of spin $\frac{1}{2}$ at lattice points

2^N possible system quantum states

$$M_j = N_+ \left(\mu_{+\frac{1}{2}}\right) + \left(N - N_+\right)\mu_{-\frac{1}{2}}$$

$$E_j(B_0) = E_j^{\circ} + N_+\left(-\mu_{+\frac{1}{2}} B_0\right) + \left(N - N_+\right)\left(-\mu_{\frac{1}{2}} B_0\right)$$

E_j°: interactions between spins in the jth system quantum state

Since spins are at distinguishable sites in the crystal, there are no restrictions about which of: $\alpha(\beta) + \beta(\alpha)$ and $\alpha(\beta) - \beta(\alpha)$ (for two of them, for example) sym. antisym. BOTH ARE ALLOWED

Work done by the sample in moving to a new position in the magnetic field is

$$dW = M\,dB_0$$

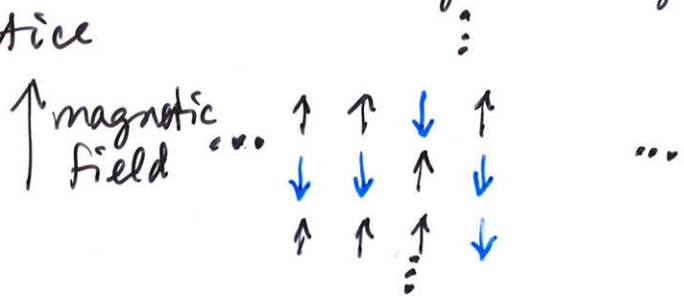
$$dE = T\,dS - M\,dB_0 \qquad dA = d(E - TS) = -S\,dT - M\,dB_0$$

$$d\left(\frac{A}{T}\right) = -\frac{E}{T^2}dT - \frac{M}{T}dB_0$$

$$E = -T^2\left[\frac{\partial (A/T)}{\partial T}\right]_{B_0}$$

ISING MODEL

Consider a system of N spins arranged on a lattice



In the presence of the magnetic field the energy of the system in a particular system quantum state is

$$E_j(B_0) = -\sum_{i=1}^{N} s_i \mu B_0 + \text{energy due to interactions between spins}$$

μ: $\frac{g\mu_B}{2}$ for example, for spin $\frac{1}{2}$

where $s_i = \pm 1$

where $s_i = \pm 1$. A simple model for the interaction energy is

$$-J \sum_{i,k}' s_i s_k$$

where J is called a coupling constant

The sum extends over NEAREST-NEIGHBOR pairs of spins.

The spin system with this interaction energy is called the Ising Model.

When $J > 0$, it is energetically favorable for neighboring spins to be aligned. Hence we might anticipate that for low enough temperature, this stabilization will lead to a cooperative phenomenon called spontaneous magnetization.

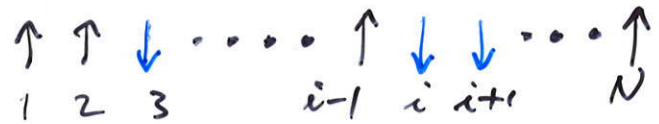
The canonical partition function is

$$Q(N,T,B_0) = \sum_j e^{-\beta E_j}$$

$$= \sum_{s_1} \sum_{s_2} \cdots \sum_{s_N = \pm 1} e^{\beta\mu B_0 \sum_{i=1}^{N} s_i + \beta J \sum_{ik}' s_i s_k}$$

The interaction term couples the different s_i's so that the multiple sums are tangled together.

In a one-dimensional lattice



the interaction energy can be reduced to a sum over a single index

$$-J \sum_{i=1}^{N} s_i s_{i+1}$$

where we have used periodic boundary conditions, that is the $N+1$ spin is the first spin. For this one-dimensional lattice,

$$Q(N,T,B_0=0) = \sum_{s_1} \sum_{s_2} \cdots \sum_{s_N} e^{\beta J \sum_{i=1}^{N} s_i s_{i+1}}$$

which at large N becomes

$$Q(N,T,B_0=0) = \left[e^{\beta J} + e^{-\beta J} \right]^N = \left[2\cosh(\beta J) \right]^N$$

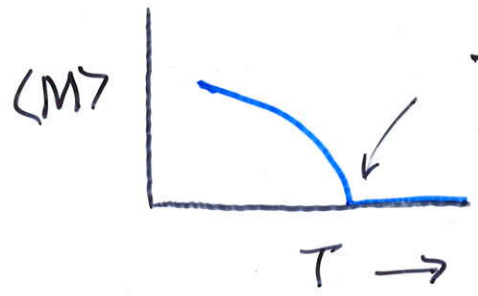
The one-dimensional model has no spontaneous magnetization, whereas the 2- and 3-D Ising model does exhibit an order-disorder phase transition. (Demonstration of this is not trivial and represents one of the major achievements of 20th century science, so says David Chandler!)

That is, through interactions between nearest neighbors, a given magnetic moment can influence the alignment of spin that are separated from the given spin by a MACROSCOPIC distance. These long-ranged correlations between spins are associated with a long-ranged order in which the lattice has a net magnetization even in the absence of a magnetic field. The magnetization in the absence of the external magnetic field

$$\langle M \rangle = \sum_{i=1}^{N} \mu s_i$$

"spontaneous magnetization"

Unless the temperature is low enough or J is high enough, there will be no net magnetization.



"critical temperature"

The system undergoes an order-disorder transition: a phase transition. Although the model is based on a magnetic system it is actually more general than that. It can be used to model mixing of two liquids for example, or liquid-gas transitions, etc.

Onsager showed that for the 2-D Ising Model,

$$Q(N, T, B_0 = 0) = \left[\left(e^{\beta J} + e^{-\beta J} \right) e^{I} \right]^N$$

where $I = \frac{1}{2\pi} \int_0^{\pi} d\phi \ln \left\{ \frac{1}{2} \left[1 + (1 - \kappa^2 \sin^2 \phi)^{1/2} \right] \right\}$

$$\kappa = \frac{2 \sinh(2\beta J)}{\cosh^2(2\beta J)}$$

and that spontaneous magnetization exists for all temperatures below

$$T_c = \frac{2.269\, J}{k_B}$$

(That is, T_c is the solution to $\sinh(2J/kT_c) = 1$)

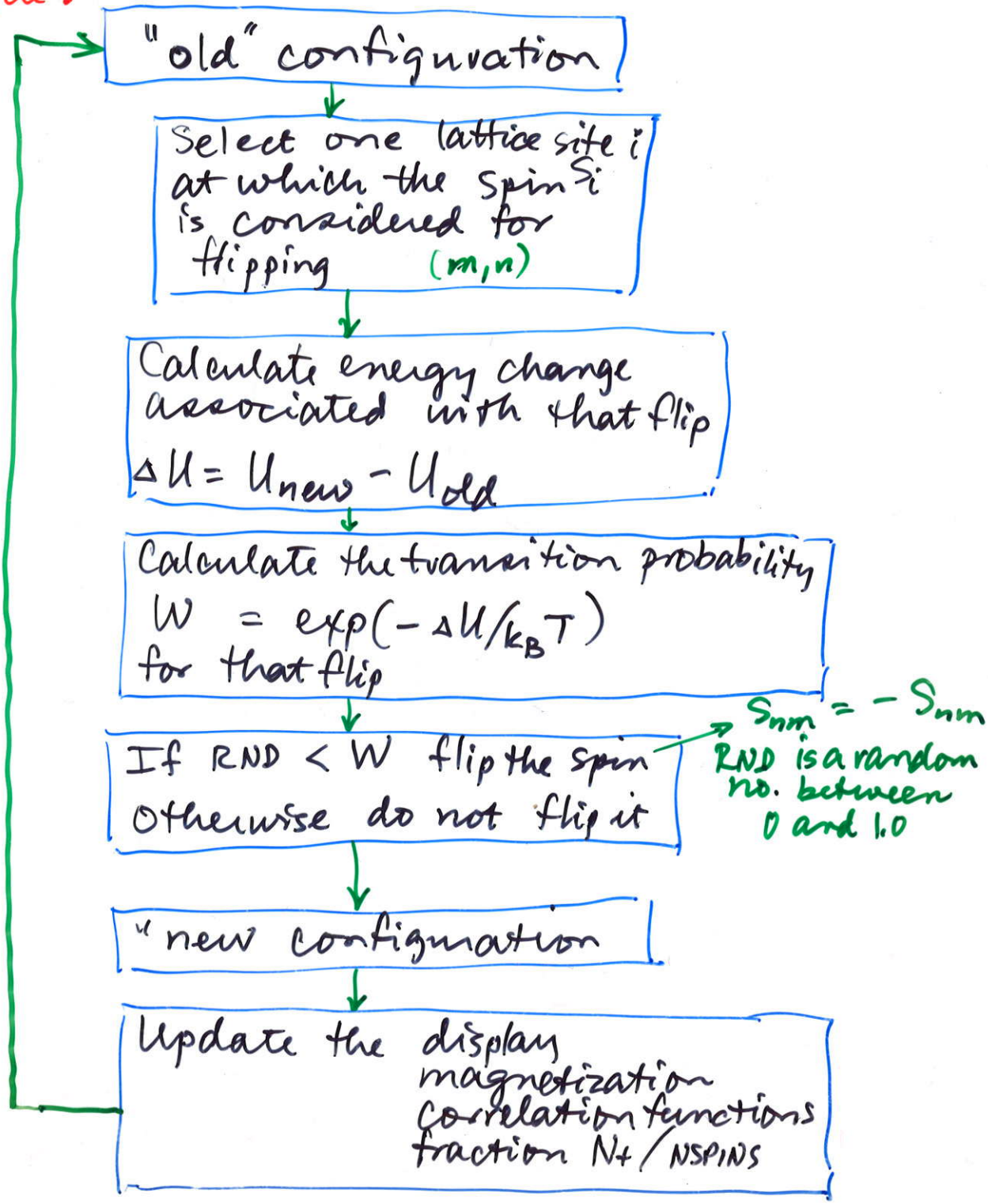
No one has solved the 3-D Ising model analytically.

DYNAMIC INTERPRETATION OF MONTE CARLO SAMPLING

Simulation of the 2-Dimensional Ising Model

- single spin flip
- Periodic boundary conditions

One cycle:



$$U_{old} = -J\, S_{n,m} * \left[S_{n-1,m} + S_{n+1,m} + S_{n,m-1} + S_{n,m+1} \right]$$

+ all others

$$U_{new} = -J\,(-S_{n,m}) * \left[S_{n-1,m} + S_{n+1,m} + S_{n,m-1} + S_{n,m+1} \right]$$

+ all others

$$\Delta U = U_{new} - U_{old}$$

$$= +2J\, S_{n,m} * \left[S_{n-1,m} + S_{n+1,m} + S_{n,m-1} + S_{n,m+1} \right]$$

Express temperature in reduced units using

$$\theta = \frac{2J}{k_B}$$

That is, actual T (Kelvins) is converted to multiples of θ according to Onsager $T_c = 2.269 \frac{J}{k_B}$ for 2-D ISING MODEL

that is, in reduced units it is $1.1345 = (T_c)_{red.}$

$$W = \exp(-\Delta U / k_B T) = \text{transition probability}$$

$$= \exp\left(- S_{n,m} * \left[S_{n-1,m} + S_{n+1,m} + S_{n,m-1} + S_{n,m+1} \right] / T_{red} \right)$$

Correlation Function is

$\langle S(0)\, S(d) \rangle$ where d is the number of lattice sites removed from origin.

How to calculate CORRELATION FUNCTION:

NSPINS = 400 — 20 x 20 grid

```
FOR M = 1 TO 5
SUMC(M) = 0
FOR I = 1 TO 20
FOR J = 1 TO 20
KJ = (J+M) MOD 20
KI = (I+M) MOD 20
MCC = S(KI, J) + S(I, KJ)
SUMC(M) = SUMC(M) + S(I,J)*MCC
NEXT J, I
PRINT M, SUMC(M)/2/NSPINS
NEXT M
```

} Periodic boundary conditions

makes contribution to correlation function be ZERO when spins are not the same

using this algorithm puts $\langle s(0)\, s(d) \rangle$ between 1.0 and ZERO.

HOW can the Ising magnet become a model for density fluctuations and liquid-gas phase transformations?

THE LATTICE GAS MODEL —

Construct a model based on a lattice, where the lattice divides space into cells. Each cell can be either occupied by a particle or unoccupied.

Let $n_i = 0$ or 1 denote the occupation number for the i^{th} cell.

The upper bound of $n_i = 1$ is effectively an excluded volume condition (no pair of particles can be closer than the lattice spacing)

Attractions between neighboring particles are accounted for in this model by saying that when particles are in nearest neighbor cells, the energy associated with each pair is $-\varepsilon$

The total energy for a given set of occupation numbers is then

$$E_{jN} = -\varepsilon \sum_{i,k}^{N_{cells}} n_i \, n_k$$

for the j^{th} system quantum state.

n_i, n_k: 0 or 1

The configuration of the system is defined by the set of occupation numbers and N = number of particles $= \sum_i^{N_{cells}} n_i$

The grand canonical partition function is given by:

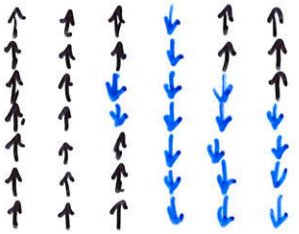
$$\mathcal{Z} = \sum_N Q_N(T,V)\, e^{\beta\mu N}$$

$$Q_N(T,V) = \sum_{jN} e^{-\beta E_{jN}}$$

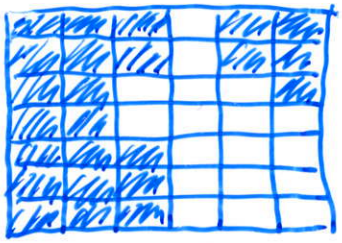
$$\mathcal{Z} = \sum_{n_1 n_2 \cdots n_{N_{cells}} = 0,1} \exp\left\{ \beta\mu \underbrace{\sum_{i=1}^{N_{cells}} n_i}_{N} + \beta\varepsilon \underbrace{\sum_{i,k}^{N_{cells}/} n_i n_k}_{-E_{jN}} \right\}$$

are possible sets of occupancies

$V = N_{cells} \times$ volume of one cell



Ising magnet



Lattice Gas

spin up $\longleftrightarrow$ occupied cell

spin down $\longleftrightarrow$ empty cell

These 2 systems are ISOMORPHIC

$s_i = 2n_i - 1$

s_i: spin, 1 or -1

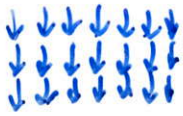
n_i: occupancy, 0 or 1

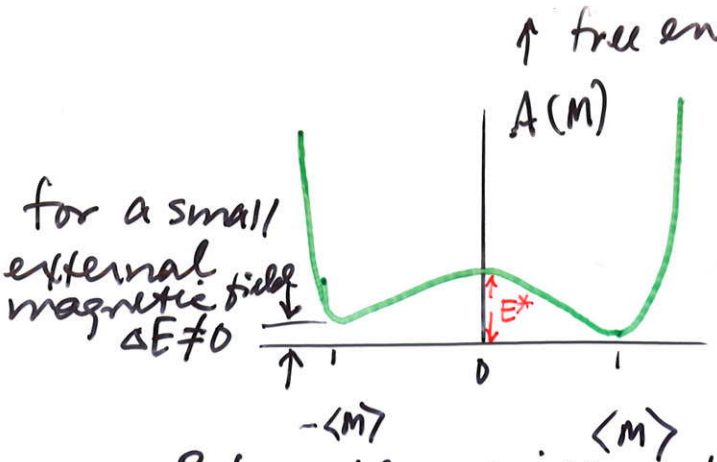
$J = \varepsilon/4$

BROKEN SYMMETRY:

In the absence of the magnetic field the Ising model is symmetric with regard to up and down directions of the spin. The ground state can be either

or





E^* is very large $\sim N^{1/2}$ for 2D
$\sim N^{2/3}$ for 3D

Below the critical temperature

The occurrence of spontaneous magnetization or the symmetry breaking associated with the long-ranged correlations results from:

Apply an external field - so the system is prepared with a magnetization of a particular sign.

Then make the external field arbitrarily weak.

If $T < T_c$ $E^* \neq 0$ spontaneous magnetization will be observed at $\langle M \rangle$ because spontaneous fluctuations will not be of sufficient size to overcome the barrier to reach a state with magnetization near $-\langle M \rangle$

ORDER PARAMETER:

For the Ising system the "order parameter" [that is, a fluctuating variable, the average value of which provides a signature of the order or broken symmetry in the system] is the fluctuating magnetization.

For the lattice gas, the "order parameter" is the deviation of the density from its critical point value.

THE RANGE OF CORRELATIONS: — The distance over which fluctuations in one region of space are correlated to those in another region. If two points are separated by a distance larger than that range, then the different fluctuations at these two points will be uncorrelated from each other.

The existence of long range order — a range of correlations that is MACROSCOPIC in size — is related to a finite value of average order parameter, that is, $\langle M \rangle \neq 0$ in the Ising system.

MAGNETIC SUSCEPTIBILITY:

For $T < T_c$ in the limit of $N_{spins} \to \infty$

$$\langle M \rangle = N_{spins}\, m_0$$

(m_0: zero external field)

$$\chi = \frac{1}{N_{spins}} \left(\frac{\partial \langle M \rangle}{\beta \partial B_0} \right)_\beta = \frac{1}{N_{spins}} \left\langle (M - \langle M \rangle)^2 \right\rangle$$

$$= \frac{\mu^2}{N_{spins}} \sum_{i,k}^{N_{spins}} \left[\langle S_i S_k \rangle - \langle S_i \rangle \langle S_k \rangle \right]$$

$$= \mu^2 N_{spins}\, m_0^2$$

χ is proportional to the mean square fluctuations in the magnetization

For $T < T_c$ there are correlations in fluctuations over MACROSCOPIC distances.

At $T = T_c$ the distinction between spin up and spin down disappears

Analogy in liquid-vapor phases: The distinction between the phases ceases to exist at the critical point

Liquid - Vapor equilibrium —

Fluctuations occur. Make observations in the volume ⋯

(a) } at temperature T well below T_c

(b) } and no gravitational field

(c) gravitational field is applied $T < T_c$

(d) the fluid at a temperature close to T_c

These are results from lattice gas model simulations in which the nearest neighbor spacing corresponds to thickness of the lines drawn.

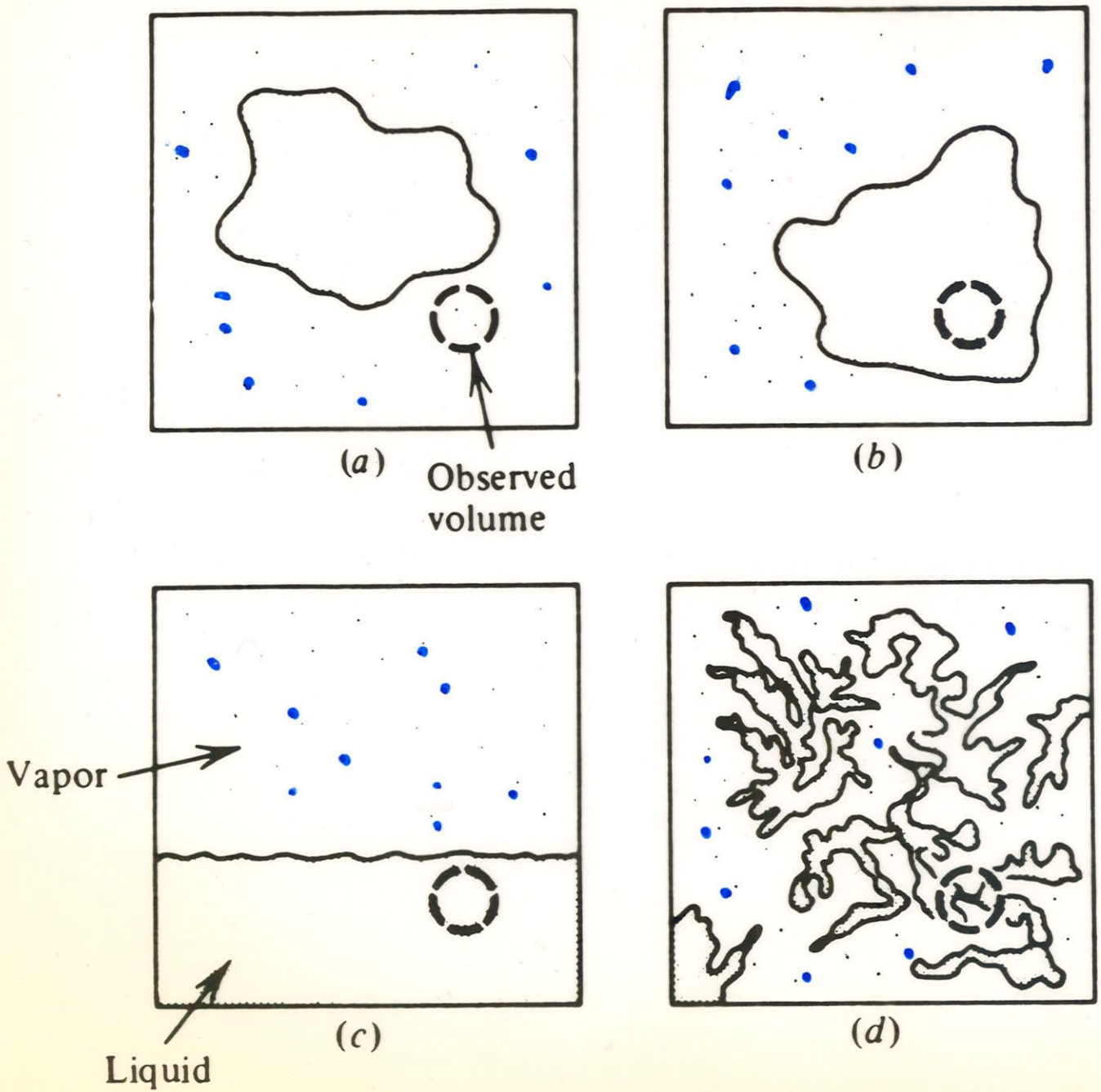


Fig. 5.7. Fluctuations with phase equilibria