

Chapter 14

Ising Model

There are many phenomena where a large number of constituents interact to give some global behavior. A magnet, for example, is composed of many interacting dipoles. A liquid is made up of many atoms. A computer program has many interacting commands. The economy, the psychology of road rage, plate tectonics, and many other things all involve phenomena where the global behavior is due to interactions between a large number of entities. One way or another, almost all such systems end up being posed as an "Ising model" of some kind. It is so common, that it is almost a joke.

The Ising model has a large number of spins which are individually in microscopic states $+1$ or -1 . The value of a spin at a site is determined by the spin's (usually short-range) interaction with the other spins in the model. Since I have explained it so vaguely, the first, and major import, of the Ising model is evident: It is the most simple nontrivial model of an interacting system. (The only simpler model would have only one possible microscopic state for each spin. I leave it as an exercise for the reader to find the exact solution of this trivial model.) Because of this, whenever one strips away the complexities of some interesting problem down to the bone, what is left is usually an Ising model of some form.

In condensed-matter physics, a second reason has been found to use the simplified-to-the-bone Ising model. For many problems where one is interested in large length scale phenomena, such as continuous phase transitions, the additional complexities can be shown to be unimportant. This is called universality. This idea has been so successful in the study of critical phenomena, that it has been tried (or simply assumed to be true) in many other contexts.

For now, we will think of the Ising model as applied to anisotropic magnets. The magnet is made up of individual dipoles which can orient up, corresponding to spin $+1$ or down corresponding to spin -1 . We neglect tilting of the spins,

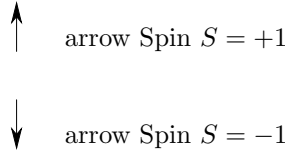
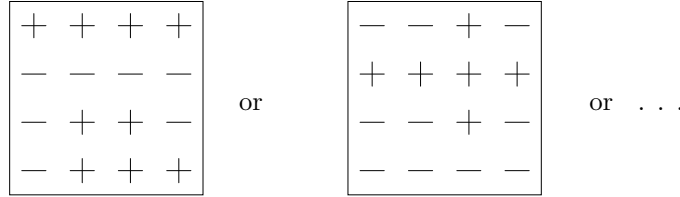


Figure 14.1:

such as \nwarrow , or \nearrow , or \searrow , and so on. For concreteness, consider dimension $d = 2$, putting all the spins on a square lattice, where there are $i = 1, 2, 3, \dots, N$ spins. In the partition function, the sum over states is

Figure 14.2: Possible configurations for a $N = 4^2 = 16$ system.

$$\begin{aligned} \sum_{\{\text{States}\}} &= \sum_{s_1=-1}^{+1} \sum_{s_2=-1}^{+1} \dots \sum_{s_N=-1}^{+1} \\ &= \prod_{i=1}^N \sum_{s_i=-1}^{+1} \end{aligned}$$

where each sum has only two terms, of course. The energy in the $\exp - E_{\text{State}}/k_B T$ now must be prescribed. Since we want to model a magnet, where all the spins are $+1$ or -1 , by and large, we make the spin of site i want to oriented the same as its neighbors. That is, for site i

$$\begin{aligned} \text{Energy of Site } i &= \sum_{\text{neighbors of } i} (S_i - S_{\text{neighbors}})^2 \\ &= S_i^2 - 2 \sum_{\text{neighbors of } i} S_i S_{\text{neigh.}} + S_{\text{neigh.}}^2 \end{aligned}$$

But $S_i^2 = 1$ always, so up to a constant (additive and multiplicative)

$$\text{Energy of Site } i = - \sum_{\text{neighbors of } i} S_i S_{\text{neighbors of } i}$$

On a square lattice, the neighbors of “ i ” are the spin surrounding it (fig. 14.3).

As said before, the idea is that the microscopic constituents -the spins- don’t know how big the system is, so they interact locally. The choice of the 4 spins

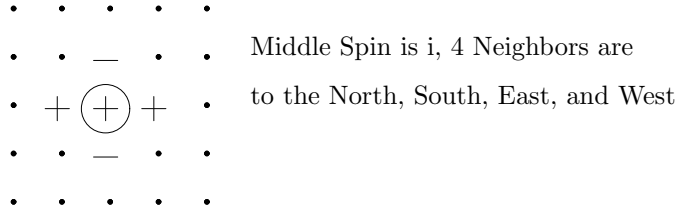


Figure 14.3: Four nearest neighbors on a square lattice.

above, below and to the *right* and *left* as “nearest neighbors” is a convention. The spins on the diagonals (NW, NE, SE, SW) are called “next-nearest neighbors”. It doesn’t actually matter how many are included, so long as the interaction is local. The total energy for all spins is

$$E_{State} = -J \sum_{\langle ij \rangle} S_i S_j$$

where J is a positive interaction constant, and $\langle ij \rangle$ is a sum over all i and $j = 1, 2, \dots, N$, provided i and j are nearest neighbors, with no double counting. Note

$$\sum_{\langle ij \rangle} = \underbrace{\sum_{i=1}^N \sum_{j=1}^N}_{\text{neighbors no double counting}} = N \times \frac{4}{2}$$

If there are “ q ” nearest neighbors, corresponding to a different interaction, or a different lattice (say hexagonal), or another dimension of space

$$\sum_{\langle ij \rangle} = \frac{q}{2} N$$

So the largest (negative) energy is $E = -\frac{qJ}{2} N$. If there is constant external magnetic field H , which tends to align spins, the total energy is

$$E_{State} = -J \sum_{\langle ij \rangle} S_i S_j - H \sum_i S_i$$

and the partition function is

$$\begin{aligned} Z &= \prod_{i=1}^N \sum_{S_i=-1}^{+1} e^{(\frac{J}{k_B T}) \sum_{\langle jk \rangle} S_j S_k + (\frac{H}{k_B T}) \sum_i S_i} \\ &= Z(N, \frac{J}{k_B T}, \frac{H}{k_B T}) \end{aligned}$$

As described above, the sum over q nearest neighbors is $q = 4$ for a two-dimensional square lattice. For three dimensions, $q = 6$ on a simple cubic lattice. The one-dimensional Ising model has $q = 2$.

The one-dimensional model was solved by Ising for his doctoral thesis (we will solve it below). The two-dimensional model was solved by Onsager, for $H = 0$, in one of the premiere works of mathematical physics. We will not give that solution. you can read it in Landau and Lifshitz's "Statistical Physics". They give a readable, physical, but still difficult treatment. The three-dimensional Ising model has not been solved.

The most interesting result of the Ising model is that it exhibits broken symmetry for $H = 0$. In the absence of a field, the energy of a state, and the partition function, have an exact symmetry

$$S_i \leftrightarrow -S_i$$

(The group is Z_2 .) Hence (?)

$$\langle S_i \rangle \leftrightarrow -\langle S_i \rangle$$

and

$$\langle S_i \rangle \stackrel{?}{=} 0$$

In fact, for dimension $d = 2$ and 3 this is not true. The exact result in $d = 2$ is surprisingly simple: The magnetization/spin is

$$m = \langle S_i \rangle = \begin{cases} (1 - \operatorname{cosech}^2 \frac{2J}{k_B T})^{1/8}, & T < T_c \\ 0, & T > T_c \end{cases}$$

The critical temperature $T_c \approx 2.269J/k_B$ is where $(1 - \operatorname{cosech}^2 \frac{2J}{k_B T})^{1/8}$ vanishes. A rough and ready understanding of this transition is easy to get. Consider the

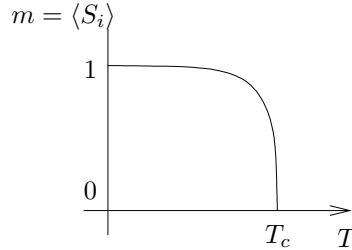


Figure 14.4: Two-dimensional square lattice Ising model magnetization per spin

Helmholtz free energy

$$F = E - TS$$

where S is *now* the entropy. At low temperatures, F is minimized by minimizing E . The largest negative value E has is $-\frac{q}{2}JN$, when all spins are aligned $+1$ or -1 . So at low temperatures (and rigorously at $T = 0$), $\langle S_i \rangle \rightarrow +1$ or $\langle S_i \rangle \rightarrow -1$. At high temperatures, entropy maximization minimizes F . Clearly entropy is maximized by having the spins helter-skelter random: $\langle S_i \rangle = 0$.

The transition temperature between $\langle S_i \rangle = 1$ and $\langle S_i \rangle = 0$ should be when the temperature is comparable to the energy per spin $k_B T = \mathcal{O}(\frac{q}{2}J)$ which is

in the right ball park. There is no hand-waving explanation for the abrupt increase of the magnetization per spin $m = \langle S_i \rangle$ at T_c . Note it is *not* like a paramagnet which shows a gradual decrease in magnetization with increasing temperature (in the presence of an external field H). One can think of it (or

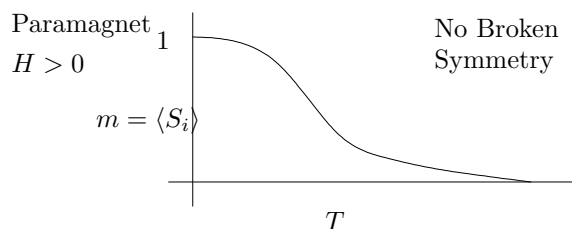


Figure 14.5:

at least remember it) this way: At T_c , one breaks a fundamental symmetry of the system. In some sense, one breaks a symmetry of nature. One can't break such a symmetry in a tentative wishy-washy way. It requires a firm, determined hand. That is, an abrupt change.

The phase diagram for the Ising model (or indeed for any magnet) look like fig. 14.6. It is very convenient that H is so intimately related with the broken

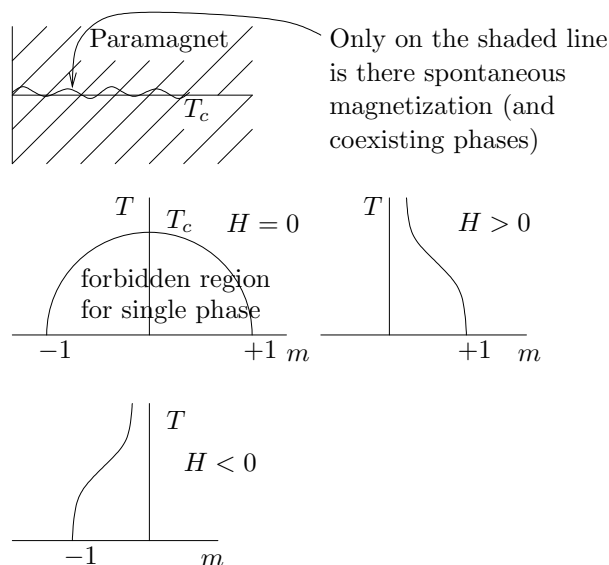


Figure 14.6:

symmetry of the Ising model. Hence it is very easy to understand that broken symmetry is for $H = 0$, not $H \neq 0$. Things are more subtle in the lattice-gas version of the Ising model.

14.1 Lattice–Gas Model

In the lattice–gas model, one still has a lattice labeled $i = 1, 2, \dots, N$, but now there is a concentration variable $c_i = 0$ or 1 at each site. The most simple model of interaction is the lattice–gas energy

$$E^{LG} = -\vartheta \sum_{\langle ij \rangle} c_i c_j - \mu \sum_i c_i$$

where ϑ is an interaction constant and μ is the constant chemical potential.

One can think of this as a model of a binary alloy (where C_i is the local concentration of one of the two phases), or a liquid–vapour system (where C_i is the local density).

This is very similar to the Ising model

$$E^{Ising} = -J \sum_{\langle ij \rangle} S_i S_j - H \sum_i S_i$$

To show they are exactly the same, let

$$S_i = 2C_i - 1$$

then

$$\begin{aligned} E^{Ising} &= -J \sum_{\langle ij \rangle} (2C_i - 1)(2C_j - 1) - H \sum_i (2C_i - 1) \\ &= -4J \sum_{\langle ij \rangle} C_i C_j + 4J \sum_{\langle ij \rangle} C_i + \text{Const.} - 2H \sum_i C_i + \text{Const.} \\ &= -4J \sum_{\langle ij \rangle} C_i C_j + 4J \frac{q}{2} \sum_i C_i - 2H \sum_i C_i + \text{Const.} \end{aligned}$$

And

$$E^{Ising} = -4J \sum_{\langle ij \rangle} C_i C_j - 2(H - J_q) \sum_i C_i + \text{Const.}$$

Since the additive constant is unimportant, this is the same as E^{LG} , provided

$$\vartheta = 4J$$

and

$$\mu = 2(H - J_q)$$

Note that the phase transition here is not at some convenient point $\mu = 0$, it is at $H = 0$, which is the awkward point $\mu = 2J_q$. This is one reason why the liquid–gas transition is sometimes said — incorrectly — to involve no change of symmetry (Z_2 group) as the Ising model. But the external field must have a carefully tuned value to get that possibility.

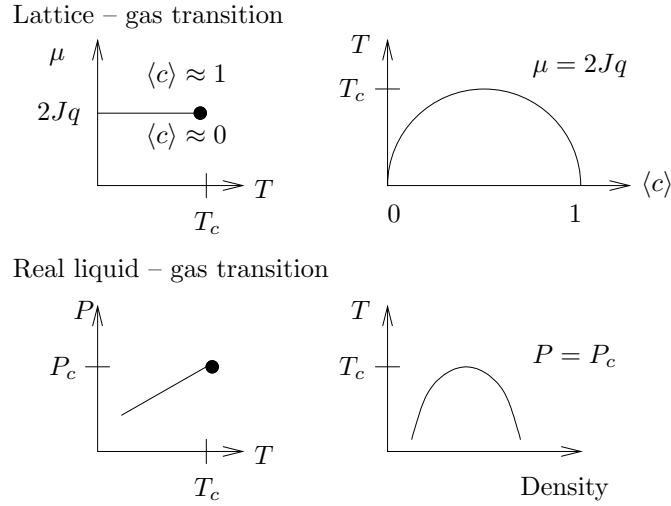


Figure 14.7:

14.2 One-dimensional Ising Model

It is easy to solve the one-dimensional Ising model. Of course, we already know that it cannot exhibit phase coexistence, from the theorem we proved earlier. Hence we expect

$$\langle S_i \rangle = m = 0$$

for all $T > 0$, where m is the magnetization per spin. The result and the method are quite useful, though.

$$Z = \prod_{i=1}^N \sum_{S_i=-1}^{+1} e^{\frac{J}{k_B T} \sum_{j=1}^N S_j S_{j+1} + \frac{H}{k_B T} \sum_{j=1}^N S_j}$$

Note we have simplified the $\sum_{\langle ij \rangle}$ for one dimension. We need, however, a prescription for the spin S_{N+1} . We will use periodic boundary conditions so that $S_{N+1} \equiv S_1$. This is called the Ising ring. You can also solve it, with a little

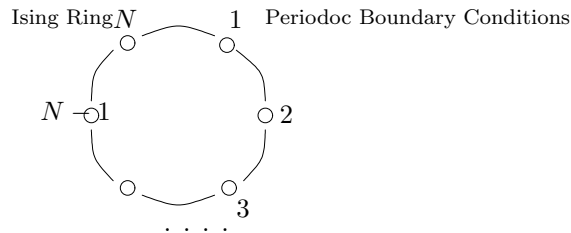


Figure 14.8:

more work, with other boundary conditions. Let the *coupling constant*

$$k \equiv J/k_B T$$

and

$$h = H/k_B T$$

be the external field. Then

$$Z(k, h, N) = \prod_{i=1}^N \sum_{S_i=-1}^{+1} e^{\sum_{j=1}^N (k S_j S_{j+1} + h S_j)}$$

or, more symmetrically,

$$\begin{aligned} Z &= \prod_{i=1}^N \sum_{S_i=-1}^{+1} e^{\sum_j [k S_j S_{j+1} + \frac{1}{2} h (S_j + S_{j+1})]} \\ &= \prod_{i=1}^N \sum_{S_i=-1}^{+1} \prod_{j=1}^N e^{k S_j S_{j+1} + \frac{1}{2} h (S_j + S_{j+1})} \end{aligned}$$

Let matrix elements of P be defined by

$$\langle S_j | P | S_{j+1} \rangle \equiv e^{k S_j S_{j+1} + \frac{1}{2} h (S_j + S_{j+1})}$$

There are only four elements

$$\begin{aligned} \langle +1 | P | +1 \rangle &= e^{k+h} \\ \langle -1 | P | -1 \rangle &= e^{k-h} \\ \langle +1 | P | -1 \rangle &= e^{-k} \\ \langle -1 | P | +1 \rangle &= e^{-k} \end{aligned}$$

Or, in matrix form,

$$P = \begin{bmatrix} e^{k+h} & e^{-k} \\ e^{-k} & e^{k-h} \end{bmatrix}$$

The partition function is

$$\begin{aligned} Z &= \prod_{i=1}^N \sum_{S_i=-1}^{+1} \langle S_1 | P | S_2 \rangle \langle S_2 | P | S_3 \rangle \dots \langle S_N | P | S_1 \rangle \\ &= \sum_{S_1=-1}^{+1} \langle S_1 | P (\sum_{S_2=-1}^{+1} | S_2 \rangle \langle S_2 |) P (\sum_{S_3=-1}^{+1} | S_3 \rangle \langle S_3 |) \dots P | S_1 \rangle \end{aligned}$$

But, clearly, the identity operator is

$$1 \equiv \sum_S | S \rangle \langle S |$$

so,

$$\begin{aligned} Z &= \sum_{S_1=-1}^{+1} \langle S_1 | P^N | S_1 \rangle \\ &= \text{Trace}(P^N) \end{aligned}$$

Say the eigenvalues of P are λ_+ and λ_- . Then,

$$Z = \lambda_+^N + \lambda_-^N$$

Finally, say $\lambda_+ > \lambda_-$. Hence as $N \rightarrow \infty$

$$Z = e^{-F/k_B T} = \lambda_+^N$$

and

$$F = -Nk_B T \ln \lambda_+$$

It remains only to find the eigenvalues of P .

We get the eigenvalues from

$$\det(\lambda - P) = 0$$

This gives

$$(\lambda - e^{k+h})(\lambda - e^{k-h}) - e^{-2k} = 0$$

or,

$$\lambda^2 - 2\lambda \left(\underbrace{\frac{e^{k+h} + e^{k-h}}{2}}_{e^k \cosh h} \right) + e^{2k} - e^{-2k} = 0$$

The solutions are

$$\begin{aligned} \lambda_{\pm} &= \frac{2e^k \cosh h \pm \sqrt{4e^{2k} \cosh^2 h - 4e^{2k} + 4e^{-2k}}}{2} \\ &= e^k [\cosh h \pm \sqrt{\cosh^2 h - 1 + e^{-4k}}] \end{aligned}$$

So,

$$\lambda_+ = e^k (\cosh h + \sqrt{\sinh^2 h + e^{-4k}})$$

is the larger eigenvalue. The free energy is

$$F = -Nk_B T [k + \ln (\cosh h + \sqrt{\sinh^2 h + e^{-4k}})]$$

where $k = J/k_B T$, and $h = H/k_B T$.

The magnetization per spin is

$$m = -\frac{1}{N} \frac{\partial F}{\partial H} = -\frac{1}{Nk_B T} \frac{\partial F}{\partial h}$$

Taking the derivative and simplifying, one obtains

$$m(h, k) = \frac{\sinh h}{\sqrt{\sinh^2 h + e^{-4k}}}$$

As anticipated, $m(h = 0, k) = 0$. There is magnetization for $h \neq 0$, although there is no broken symmetry of course. There is a phase transition at $T = 0$.

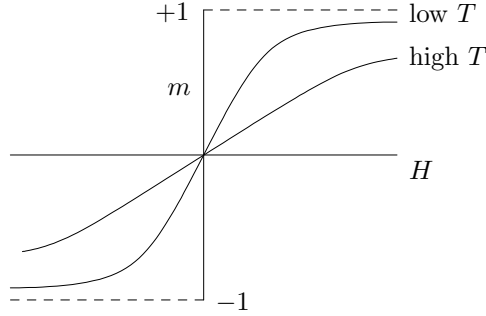


Figure 14.9: Magnetization of 1-d Ising model

14.3 Mean-Field Theory

There is a very useful approximate treatment of the Ising model. We will now work out the most simple such “mean-field” theory, due in this case to Bragg and Williams.

The idea is that each spin is influenced by the local magnetization, or equivalently local field, of its surrounding neighbors. In a magnetized, or demagnetized state, that local field does not fluctuate very much. Hence, the idea is to replace the local field, determined by a local magnetization, with an average field, determined by the average magnetization. “Mean” field means average field, not nasty field.

It is easy to solve the partition function if there is only a field, and no interactions. This is a (very simple) paramagnet. Its energy is

$$E_{State} = -H \sum_i S_i$$

and,

$$\begin{aligned} Z &= \prod_i \sum_{S_i = -1}^{+1} e^{\frac{H}{k_B T} \sum_j S_j} \\ &= \left(\sum_{S_1 = \pm 1} e^{\frac{H}{k_B T} S_1} \right) \dots \left(\sum_{S_N = \pm 1} e^{\frac{H}{k_B T} S_N} \right) \\ &= \left(\sum_{S = \pm 1} e^{\frac{H}{k_B T} S} \right)^N \end{aligned}$$

so,

$$Z = \left(2 \cosh \frac{H}{k_B T} \right)^N$$

and

$$F = -N k_B T \ln 2 \cosh \frac{H}{k_B T}$$

so since,

$$m = -\frac{1}{N} \partial F / \partial H$$

then

$$m = \tanh H / k_B T$$

For the interacting Ising model we need to find the effective local field H_i at

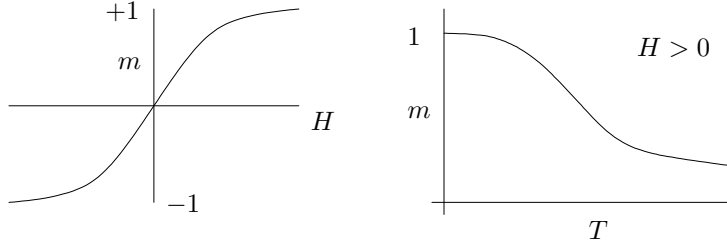


Figure 14.10: Noninteracting paramagnet solution

site i . The Ising model is

$$E_{State} = -J \sum_{\langle ij \rangle} S_i S_j - H \sum_i S_i$$

we want to replace this — in the partition function weighting — with

$$E_{State} = - \sum_i H_i S_i$$

Clearly

$$-\frac{\partial E}{\partial S_i} = H_i$$

Thus, from the Ising model

$$\begin{aligned} -\frac{\partial E}{\partial S_i} &= J \sum_{\langle jk \rangle} (S_j \delta_{k,i} + \delta_{j,i} S_k) + H \\ &= J \cdot 2 \cdot \sum_{\substack{j \text{ neighbors of } i \\ \text{(no double counting)}}} S_j + H \end{aligned}$$

Now let's get rid of the 2 and the double-counting restriction. Then

$$H_i = J \sum_{j \text{ neighbors of } i} S_j + H$$

is the effective local field. To do mean-field theory we let

$$H_i \approx \langle H_i \rangle$$

where

$$\langle H_i \rangle = J \sum_{j \text{ neighbors}} \langle S_j \rangle + H$$

but all spins are the same on average, so

$$\langle H_i \rangle = qJ\langle S \rangle + H$$

and the weighting of states is given by

$$E_{State} = - \underbrace{(qJ\langle S \rangle + H)}_{\text{mean field, } \langle H \rangle} \sum_i S_i$$

For example, the magnetization is

$$m = \langle S \rangle = \frac{\sum_{S=\pm 1} S e^{\frac{\langle H \rangle}{k_B T} S}}{\sum_{S=\pm 1} e^{\frac{\langle H \rangle}{k_B T} S}}$$

where $\langle S \rangle = \langle S_1 \rangle$, and contributions due to $S_2, S_3 \dots$ cancel from top and bottom. So

$$m = \tanh \frac{\langle H \rangle}{k_B T}$$

or

$$m = \tanh \frac{qJm + H}{k_B T}$$

This gives a critical temperature

$$k_B T_c = qJ$$

as we will now see.

Consider $H = 0$.

$$m = \tanh \frac{m}{T/T_c}$$

Close to T_c , m is close to zero, so we can expand the tanh function:

$$m = \frac{m}{T/T_c} - \frac{1}{3} \frac{m^3}{(T/T_c)^3} + \dots$$

One solution is $m = 0$. This is stable above T_c , but unstable for $T < T_c$. Consider $T < T_c$, where m is small, but nonzero. Dividing by m gives

$$1 = \frac{1}{T/T_c} - \frac{1}{3} \frac{m^2}{(T/T_c)^3} + \dots$$

Rearranging

$$m^2 = 3\left(\frac{T}{T_c}\right)^2\left(1 - \frac{T}{T_c}\right) + \dots$$

Or,

$$m = \left(3\frac{T}{T_c}\right)^{1/2}\left(1 - \frac{T}{T_c}\right)^{1/2}$$

for small m , $T < T_c$. Note that this solution does not exist for $T > T_c$. For $T < T_c$, but close to T_c , we have

$$m \propto \left(1 - \frac{T}{T_c}\right)^\beta$$

where the critical exponent, $\beta = 1/2$. All this is really saying is that m is a

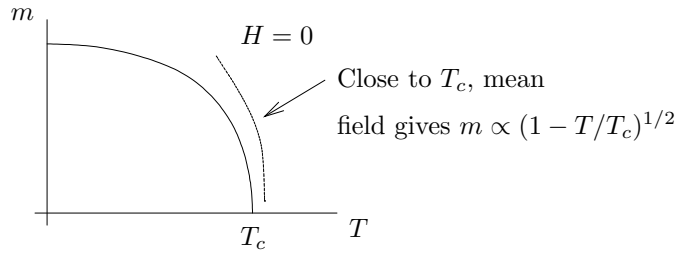


Figure 14.11:

parabola near T_c , as drawn in fig. 14.12 (within mean field theory). This is

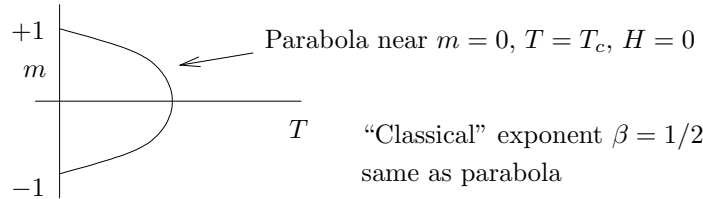


Figure 14.12:

interesting, and useful, and easy to generalize, but only qualitatively correct. Note

$$k_B T_c = qJ = \begin{cases} 2J & , d = 1 \\ 4J & , d = 2 \\ 6J & , d = 3 \end{cases}$$

The result for $d = 1$ is wildly wrong, since $T_c = 0$. In $d = 2$, $k_B T_c \approx 2.27J$, so the estimate is poor. Also, if we take the exact result from Onsager's solution,

$m \propto (1 - T/T_c)^{1/8}$, so $\beta = 1/8$ in $d = 2$. In three dimensions $k_B T_c \sim 4.5J$ and estimates are $\beta = 0.313\dots$. Strangely enough, for $d \geq 4$, $\beta = 1/2$ (although there are logarithmic corrections in $d = 4$)!

For $T \equiv T_c$, but $H \neq 0$, we have

$$m = \tanh\left(m + \frac{H}{k_B T_c}\right)$$

or

$$H = k_B T_c (\tanh^{-1} m - m)$$

Expanding giving

$$H = k_B T_c \left(m + \frac{1}{3}m^3 + \dots - m\right)$$

so

$$H = \frac{k_B T_c}{3} m^3$$

for m close to zero, at $T = T_c$. This defines another critical exponent

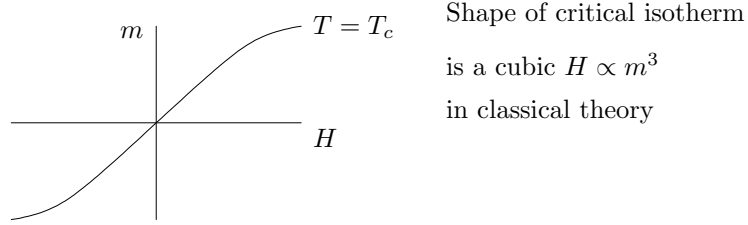


Figure 14.13:

$$H \propto m^\delta$$

for $T = T_c$, where $\delta = 3$ in mean-field theory.

The susceptibility is

$$X_T \equiv \left(\frac{\partial m}{\partial H}\right)_T$$

This is like the compressability in liquid-gas systems

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$$

Note the correspondence between density and magnetization per spin, and between pressure and field. The susceptibility “asks the question”: how easy is it to magnetize something with some small field. A large X_T means the material is very “susceptible” to being magnetized.

Also, as an aside, the “sum rule” for liquids

$$\int d\vec{r} \langle \Delta n(r) \Delta n(0) \rangle = n^2 k_B T \kappa_T$$

has an analog for, magnets

$$\int d\vec{r} \langle \Delta m(r) \Delta m(0) \rangle \propto X_T$$

We do not need the proportionality constant.

From above, we have

$$m = \tanh \frac{k_B T_c m + H}{k_B T}$$

or,

$$H = k_B T \cdot \tanh^{-1} m - k_B T_c m$$

and

$$\left(\frac{\partial H}{\partial m} \right)_T = k_B T \frac{1}{1 - m^2} - k_B T_c$$

so

$$X_T = \frac{1}{T - T_c}$$

close to T_c . Or

$$X_T \propto |T - T_c|^{-\gamma}$$

where $\gamma = 1$. This is true for $T \rightarrow T_c^+$, or, $T \rightarrow T_c^-$. To get the energy, and so

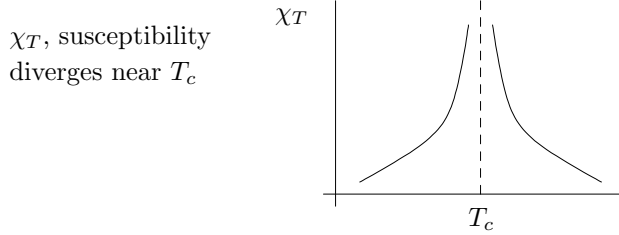


Figure 14.14:

the heat capacity, consider

$$\langle E \rangle = \left\langle -J \sum_{\langle ij \rangle} S_i S_j - H \sum_i S_i \right\rangle$$

All the spins are independent, in mean-field theory, so

$$\langle S_i S_j \rangle = \langle S_i \rangle \langle S_j \rangle$$

Hence

$$\langle E \rangle = -\frac{Jq}{2} N m^2 - H N m$$

The specific heat is

$$c = \frac{1}{N} \left(\frac{\partial E}{\partial T} \right)_N$$

Near T_c , and at $H = 0$,

$$m^2 \propto \begin{cases} (T_c - T) & T < T_c \\ 0 & T > T_c \end{cases}$$

So,

$$\langle E \rangle = \begin{cases} -(Const.)(T_c - T), & T < T_c \\ 0, & T > T_c \end{cases}$$

and

$$c = \begin{cases} Const. & T < T_c \\ 0 & T > T_c \end{cases}$$

If we include temperature dependence away from T_c , the specific heat looks more like a saw tooth, as drawn in fig. 14.15. This discontinuity in c , a second

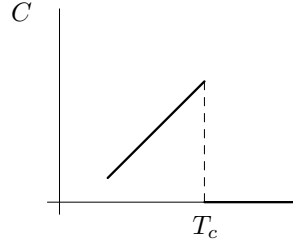


Figure 14.15: Discontinuity in C in mean field theory.

derivative of the free energy is one reason continuous phase transitions were called “second order”. Now it is known that this is an artifact of mean field theory.

It is written as

$$c \propto |T - T_c|^{-\alpha}$$

where the critical exponent

$$\alpha = o(disc.)$$

To summarize, near the critical point,

$$\begin{aligned} m &\sim (T_c - T)^\beta, & T < T_c, H = 0 \\ H &\sim m^\delta, & T = T_c \\ X_T &\sim |T - T_c|^{-\gamma}, & H = 0 \end{aligned}$$

and

$$c \sim |T - T_c|^{-\alpha}, \quad H = 0$$

The exponents are:

	mean field	$d = 2$ (exact)	$d = 3$ (num)	$d \geq 4$
α	0 (disc.)	0 (log)	0.125...	0 (disc.)
β	1/2	1/8	0.313...	1/2
γ	1	7/4	1.25...	1
δ	3	15	5.0...	3

Something is happening at $d = 4$. We will see later that mean-field theory works for $d \geq 4$. For now we will leave the Ising model behind.

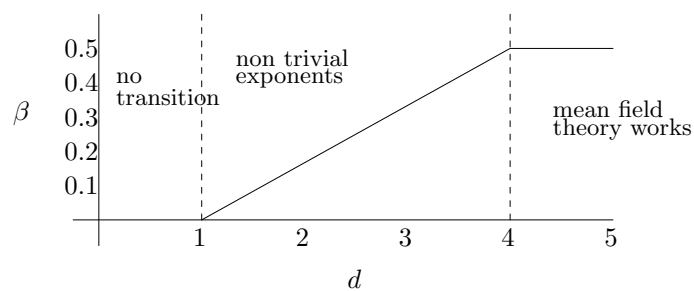


Figure 14.16: Variation of critical exponent β with spatial dimension

Chapter 5

Molecular Dynamics

At this point, one might say, computers are so big and fierce, why not simply solve the microscopic problem completely! This is the approach of molecular dynamics. It is a very important numerical technique, which is very very conservative. It is used by physicists, chemists, and biologists.

Imagine a classical solid, liquid or gas composed of many atoms or molecules. Each atom has a position \vec{r}_i and a velocity \vec{v}_i (or momentum $m\vec{v}_i$). The Hamil-

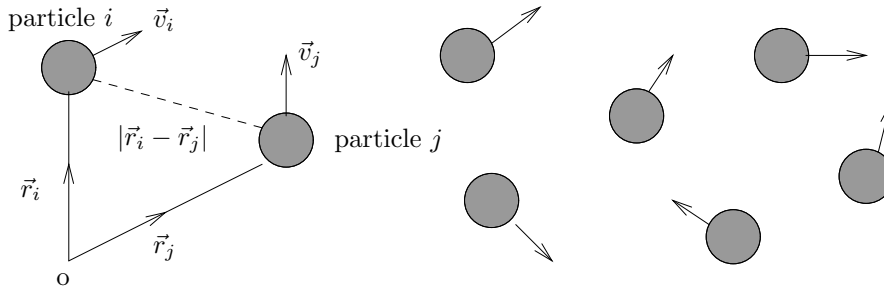


Figure 5.1:

tonian is (where m is the atom's mass)

$$H = \sum_{i=1}^N \frac{m\vec{v}_i^2}{2} + V(\vec{r}_1, \dots, \vec{r}_N)$$

Usually, the total potential can be well approximated as the sum of pairwise forces, i.e.

$$V(r_1, \dots, r_N) = \sum_{\substack{i=1, j=1 \\ (i>j)}}^N V(|\vec{r}_i - \vec{r}_j|)$$

which only depends on the distance between atoms. This potential usually has

a form like that drawn. Where the depth of the well must be

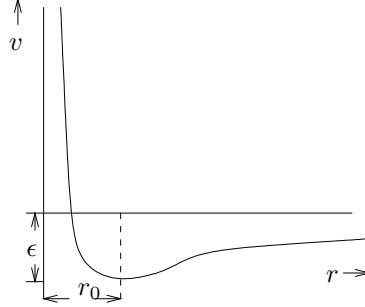


Figure 5.2:

$$\epsilon \sim (100's\ K)k_B$$

and

$$r_o \sim (a\ few\ \text{\AA})$$

This is because, in a vapor phase, the density is small and the well is unimportant; when the well becomes important, the atoms condense into a liquid phase. Hence $\epsilon \sim$ boiling point of a liquid, and r_o is the separation of atoms in a liquid. Of course, say the mass of an atom is

$$m \sim 10 \times 10^{-27} kg$$

$$r_o \sim 2\text{\AA}$$

then the liquid density is

$$\begin{aligned} \rho &\sim \frac{m}{r_o^3} = \frac{10 \times 10^{-27} kg}{10\text{\AA}^3} \\ &= \frac{10^{-27} \times (10^3 gm)}{(10^{-8} cm)^3} \\ \rho &\sim 1 gm/cm^3 \end{aligned}$$

of course. To convince oneself that quantum effects are unimportant, simply estimate the de Broglie wavelength

$$\begin{aligned} \lambda &\sim \frac{\hbar}{\sqrt{mk_B T}} \\ &\sim 1\text{\AA}/\sqrt{T} \end{aligned}$$

where T is measured in Kelvin. So this effect is unimportant for most liquids. The counter example is Helium. In any case, quantum effects are usually

marginal, and lead to no quantitative differences of importance. This is simply because the potentials are usually parameterized fits such as the Lennard - Jones potential

$$V(r) = 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6]$$

where

$$r_o = 2^{1/6}\sigma \approx 1.1\sigma$$

and

$$V(r_o) = -\epsilon$$

by construction. For Argon, a good “fit” is

$$\begin{aligned} r_o &= 3.4\text{\AA} \\ \epsilon &= 120K \end{aligned}$$

Numerically it is convenient that $V(2r_o) \ll \epsilon$, and is practically zero. Hence one usually considers

$$V(r) = \begin{cases} \text{Lennard - Jones} & , r < 2r_o \\ 0 & , r > 2r_o \end{cases}$$

where $r_o = 2^{1/6}\sigma$. Lennard-Jones has a run-of-the-mill phase diagram which is representative of Argon or Neon, as well as most simple run-of-the-mill pure substances. Simpler potentials like the square well also have the same properties.

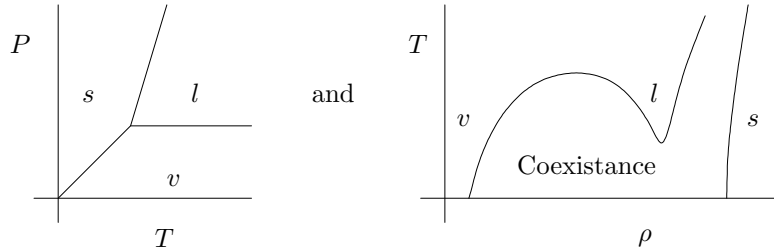


Figure 5.3: Leonnard Jousium (The solid phase is fcc as I recall)

But the hard sphere potential has a more simple-minded phase diagram. This

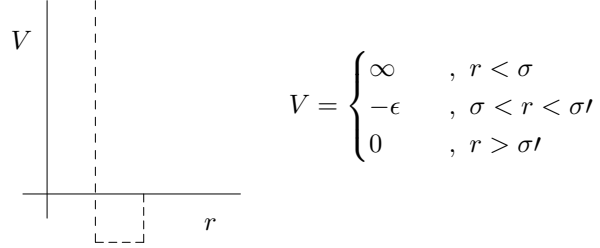
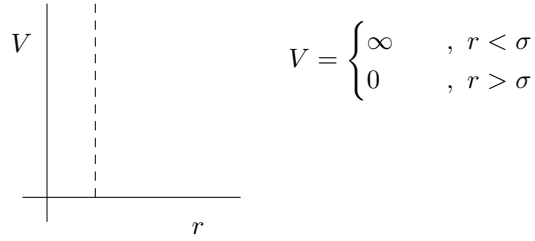


Figure 5.4:



where,

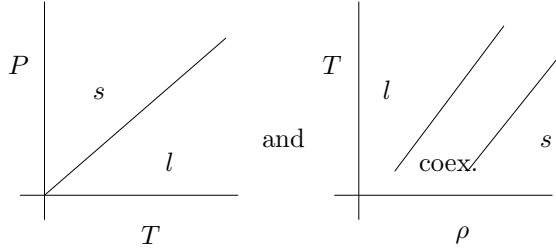


Figure 5.5:

is because of the lack of an attractive interaction.

Finally, let's get to the molecular dynamics method. Newton's equations (or Hamilton's) are,

$$\frac{d\vec{r}_i}{dt} = \vec{v}_i$$

and $\vec{a}_i = \frac{\vec{F}_i}{m}$

$$\frac{d\vec{v}_i}{dt} = \frac{1}{m} \sum_{\substack{j=1 \\ (i \neq j)}}^N \frac{\partial}{\partial \vec{r}_i} V(|\vec{r}_i - \vec{r}_j|)$$

Clearly, we can simply solve these numerically given all the positions and velocities initially, i.e. $\{\vec{r}_i(t=0), \vec{v}_i(t=0)\}$. A very simple (in fact too simple) way

to do this is by

$$\frac{d\vec{r}_i}{dt} = \frac{\vec{r}_i(t + \Delta t) - \vec{r}_i}{\Delta t}$$

for small Δt . This gives

$$\vec{r}_i(t + \Delta t) = \vec{r}_i(t) + \Delta t \vec{v}_i(t)$$

and

$$\vec{r}_i(t + \Delta t) = \vec{v}_i(t) + \Delta t \frac{1}{m} \vec{F}_i$$

where $\vec{F}_i(t)$ is determined by $\{\vec{r}_i(t)\}$ only. A better (but still simple) method is due to Verlet. It should be remembered that the discretization method has a little bit of black magic in it.

Valet notes that,

$$\vec{r}_i(t \pm \Delta t) = \vec{r}_i(t) \pm \Delta t \vec{v}_i + \frac{(\Delta t)^2}{2} \vec{a}_i(t) + \dots$$

where $\vec{a}_i = \vec{F}_i/m = \frac{d^2 \vec{r}_i}{dt^2}$. Add this to itself

$$\vec{r}_i(t + \Delta t) = 2\vec{r}_i(t) - \vec{r}_i(t - \Delta t) + (\Delta t)^2 \frac{1}{m} \vec{F}_i + \mathcal{O}(\Delta t)$$

And us the simple rule

$$\vec{v}_i(t + \Delta t) = \frac{\vec{r}_i(t + \Delta t) - \vec{r}_i(t - \Delta t)}{2\Delta t}$$

Thats all. You have to keep one extra set of \vec{r}_i 's, but it is the common method, and works well. To do statistical mechanics, you do time averages, after the system equilibrates. Or ensemble averages over different initial conditions. The ensemble is microcanonical since energy is fixed. Usually one solves it for a fixed volume, using periodic boundary conditions. A common practice is to do a

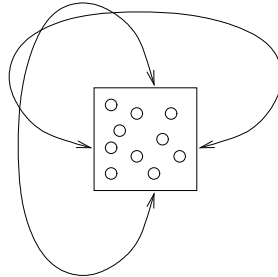


Figure 5.6: Periodic Boundary Conditions

“canonical” ensemble by fixing temperature through the sum rule

$$\frac{1}{2}m\langle v^2 \rangle = \frac{1}{2}k_B T$$

or,

$$T = \frac{\langle v^2 \rangle}{mk_B}$$

This is done by constantly rescaling the magnitude of the velocities to be

$$|v| \equiv \langle v^2 \rangle^{1/2} \equiv \sqrt{mk_B T}$$

What about microscopic reversibility and the arrow of time?

Recall the original equations

$$\frac{\partial \vec{r}_i}{\partial t} = \vec{v}_i$$

$$\frac{\partial \vec{v}_i}{\partial t} = \frac{1}{m} \sum_{\substack{j \\ (j \neq i)}} \frac{\partial}{\partial \vec{r}_i} V(|r_i - r_j|)$$

The equations are invariant under time reversal $t \rightarrow -t$ if

$$\begin{aligned} \vec{r} &\rightarrow \vec{r} \\ \vec{v} &\rightarrow -\vec{v} \end{aligned}$$

How then can entropy increase? This is a deep and uninteresting question. Entropy does increase; it's a law of physics. The real question is how to calculate how *how fast* entropy increases; e.g. calculate a viscosity or a diffusion constant, which set the time scale over which entropy increases.

Nevertheless, here's a neat way to fool around with this a bit. Take a gas of N atoms in a box of size L^d where energy is fixed such that the average equilibrium separation between atoms

$$s_{eq} = \mathcal{O}(3 \text{ or } 4)r_o$$

where r_o is a parameter giving the rough size of the atoms. Now initialize the atoms in a corner of the box with

$$s(t=0) = \mathcal{O}(r_o)$$

or smaller (see fig. 5.7). Now, at time $t = \text{later}$, let all $\vec{v} \rightarrow -\vec{v}$. By microscopic reversibility you should get fig. 5.8. Try it! You get fig. 5.9. It is round off

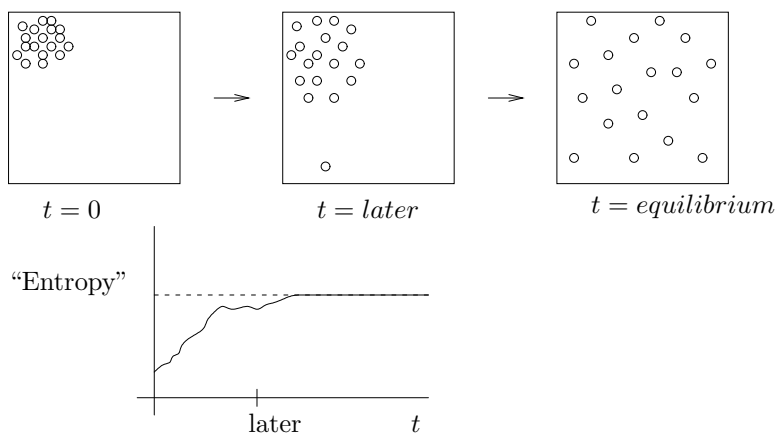


Figure 5.7:

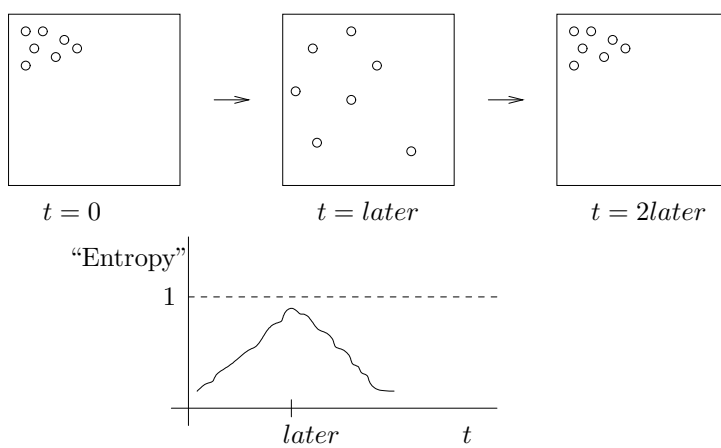


Figure 5.8:

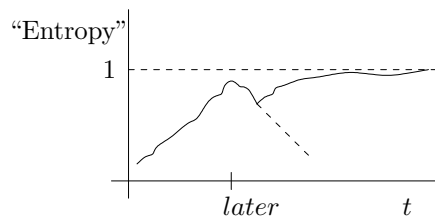


Figure 5.9:

error, but try to improve your precision. *You will always get the same thing.* Think about it. The second law is a law, not someone's opinion.

Chapter 6

Monte Carlo and the Master Equation

An important description for nonequilibrium statistical mechanics is provided by the master equation. This equation also provides the motivation for the Monte Carlo method, the most important numerical method in many-body physics.

The master equation, despite the pretentious name, is phenomenology following from a few reasonable assumptions. Say a system is defined by a state $\{S\}$. This state might, for example, be all the spins ± 1 that an Ising model has at each site. That is $\{S\}$ are all the states appearing in the

$$Z = \sum_{\{S\}} e^{-E\{S\}/k_B T} \quad (6.1)$$

partition function above. We wish to know the probability of being in some state $\{S\}$ at a time t ,

$$p(\{S\}, t) = ? \quad (6.2)$$

from knowledge of probabilities of states at earlier times. In the canonical ensemble (fixed T , fixed number of particles)

$$P_{eq}(\{S\}) \propto e^{-E\{S\}/k_B T} \quad (6.3)$$

of course. For simplicity, let's drop the $\{ \}$ brackets and let

$$\{S\} \equiv S \quad (6.4)$$

As time goes on, the probability of being in state S *increases* because one makes transitions *into* this state from other (presumably nearby in some sense) states S' . Say the probability of going from $S \rightarrow S'$, in a unit time is

$$W(S, S') \equiv_{(\text{Read As})} W(S \leftarrow S') \quad (6.5)$$

This is a transition rate as shown in fig. 6.1. Hence

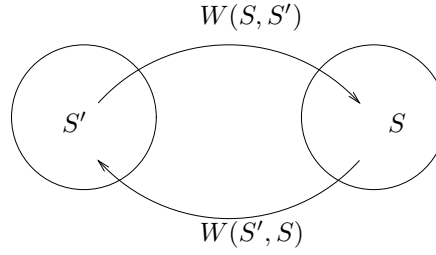


Figure 6.1:

$$W(S, S') P(S') \quad (6.6)$$

are contributions increasing $P(S)$.

However, $P(S)$ *decreases* because one makes transitions *out* of S to the states S' with probability

$$W(S', S) \underset{\text{(Read As)}}{\equiv} W(S' \leftarrow S) \quad (6.7)$$

So that

$$W(S', S) P(S) \quad (6.8)$$

are contributions decreasing $P(S)$ as time goes on.

The master equation incorporates both these processes as

$$\frac{\partial P(S, t)}{\partial t} = \sum_{S'} [W(S, S') P(S') - W(S', S) P(S)] \quad (6.9)$$

which can be written as

$$\frac{\partial P(S, t)}{\partial t} = \sum_{S'} L(S, S') P(S') \quad (6.10)$$

where the inappropriately named Liouvillian is

$$L(S, S') = W(S, S') - \left(\sum_{S''} W(S'', S) \right) \delta_{S, S'} \quad (6.11)$$

Note that the master equation

1. has no memory of events further back in time than the differential element “ dt ”. This is called a Markov process
2. is linear.
3. is not time reversal invariant as $t \rightarrow -t$ (since it is first order in time).

In equilibrium,

$$\frac{\partial P_{eq}(S)}{\partial t} = 0 \quad (6.12)$$

since we know this to be the definition of equilibrium. Hence in Eq. 6.9,

$$W(S, S') P_{eq}(S') = W(S', S) P_{eq}(S) \quad (6.13)$$

which is called detailed balance of transitions or fluctuations. For the canonical ensemble therefore,

$$\frac{W(S, S')}{W(S', S)} = e^{-(E(S) - E(S'))/k_B T} \quad (6.14)$$

This gives a surprisingly simple result for the transitions W , it is necessary (but not sufficient) that they satisfy Eq. 6.14. In fact, if we are only concerned with equilibrium properties, *any* W which satisfies detailed balance is allowable. We need only pick a convenient W !

The two most common W 's used in numerical work are the metropolis rule

$$W_{Metropolis}(S, S') = \begin{cases} e^{-\Delta E/k_B T} & , \Delta E > 0 \\ 1 & , \Delta E \leq 0 \end{cases} \quad (6.15)$$

and the Glauber rule

$$W_{Glauber}(S, S') = \frac{1}{2} (1 - \tanh \frac{\Delta E}{2k_B T}) \quad (6.16)$$

where

$$\Delta E = E(S) - E(S') \quad (6.17)$$

Let us quickly check that $W_{Metropolis}$ satisfies detailed balance. If $E(S) > E(S')$

$$\frac{W(S, S')}{W(S', S)} = \frac{e^{-(E(S) - E(S'))/k_B T}}{1} = e^{-\Delta E/k_B T}$$

Now if $E(S) < E(S')$

$$\frac{W(S, S')}{W(S', S)} = \frac{1}{e^{-(E(S) - E(S'))/k_B T}} = e^{-\Delta E/k_B T}$$

where $\Delta E = E(S) - E(S')$ as above. So Detailed balance works. You can check yourself that the Glauber rule works. The form of the rule is shown in figures 6.2 and 6.3. To do numerical work via Monte Carlo, we simply make transitions from state $\{S'\} \rightarrow \{S\}$ using the probability $W(\{S\}, \{S'\})$. A last bit of black magic is that one usually wants the states $\{S'\}$ and $\{S\}$ to be “close”. For something like the Ising model, a state $\{S\}$ is close to $\{S'\}$ if the two states differ by no more than one spin flip, as drawn in fig. 6.4. Let us do this explicitly for the 2 dimensional Ising model in zero field, the same thing that Onsager solved!

$$E_{STATE} = -J \sum_{\langle ij \rangle} S_i S_j \quad (6.18)$$

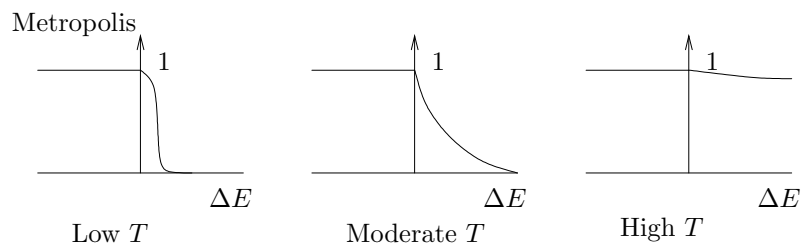


Figure 6.2:

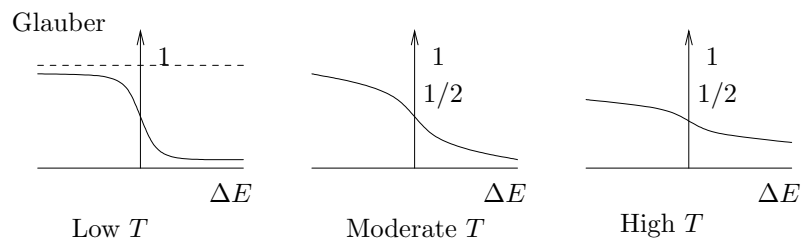


Figure 6.3:

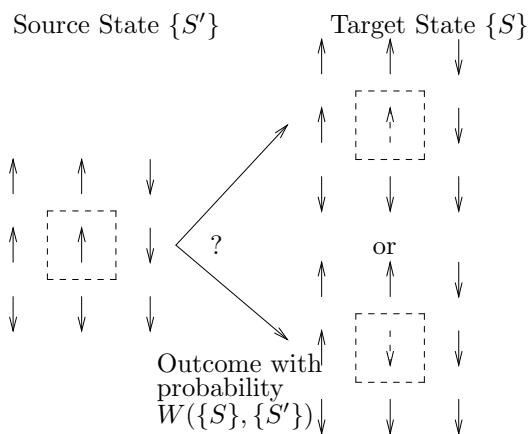


Figure 6.4:

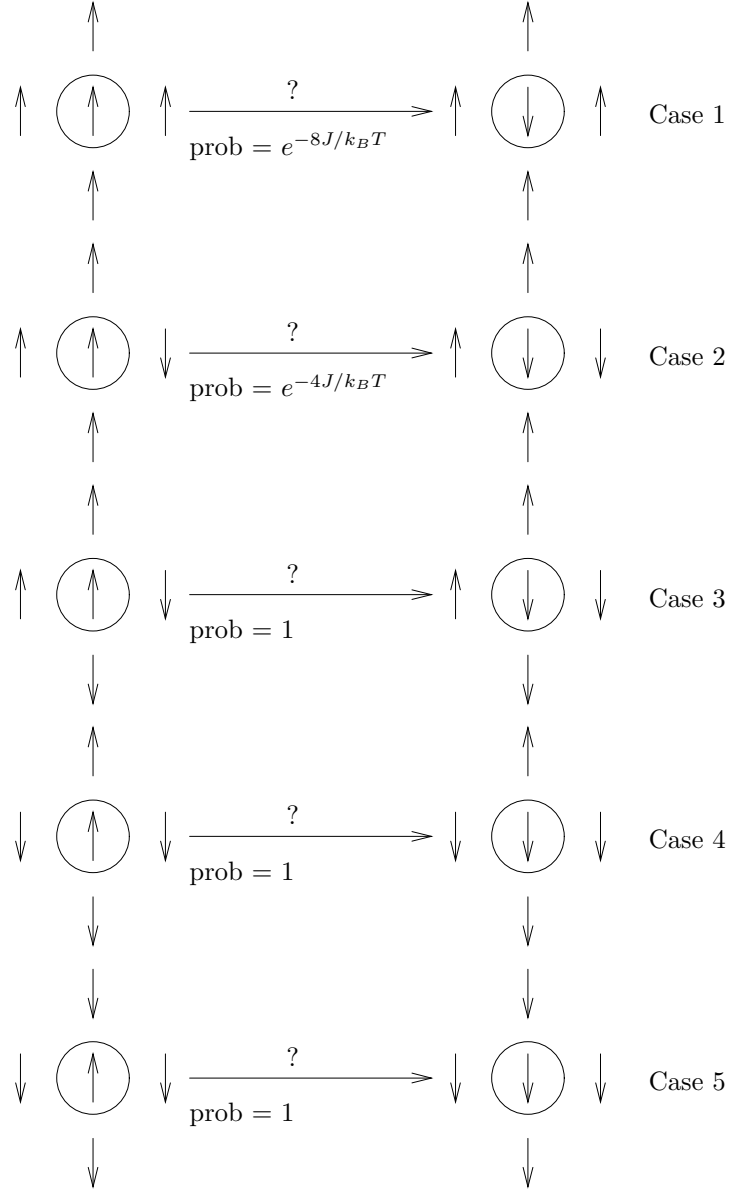


Figure 6.5:

where $S_i = \pm 1$ are the spins on sites $i = 1, 2, \dots, N$ spins (not to be confused with our notation for a state $\{S\}$!), and $\langle ij \rangle$ means only nearest neighbours are summed over. The positive constant J is the coupling interaction. *If only one spin can possibly flip, note there are only five cases to consider as shown in fig. 6.5.*

To get the probabilities (Metropolis)

For Case 1:

$$\begin{aligned} E_{Before} &= -4J \quad , \quad E_{After} = +4J \\ \Delta E &= 8J \\ W(S, S') &= \text{Prob. of flip} = e^{-8J/k_B T} \end{aligned}$$

For Case 2:

$$\begin{aligned} E_{Before} &= -2J \quad , \quad E_{After} = +2J \\ \Delta E &= 4J \\ W(S, S') &= \text{Prob. of flip} = e^{-4J/k_B T} \end{aligned}$$

For Case 3:

$$\begin{aligned} E_{Before} &= 0 \quad , \quad E_{After} = 0 \\ \Delta E &= 0 \\ W(S, S') &= \text{Prob. of flip} = 1 \end{aligned}$$

For Case 4:

$$\begin{aligned} E_{Before} &= +2J \quad , \quad E_{After} = -2J \\ \Delta E &= -4J \\ W(S, S') &= \text{Prob. of flip} = 1 \end{aligned}$$

For Case 5:

$$\begin{aligned} E_{Before} &= +4J \quad , \quad E_{After} = -4J \\ \Delta E &= -8J \\ W(S, S') &= \text{Prob. of flip} = 1 \end{aligned}$$

This is easy if $W = 1$, if $W = e^{-4J/k_B T}$, then you have to know the temperature in units of J/k_B . Let's say, for example,

$$W = 0.1$$

You know the spin flips 10% of the time. You can enforce this by comparing $W = 0.1$ to a random number uniformly between 0 and 1. If the random number is less than or equal to W , then you flip the spin.

Here is an outline of a computer code. If you start at a large temperature and

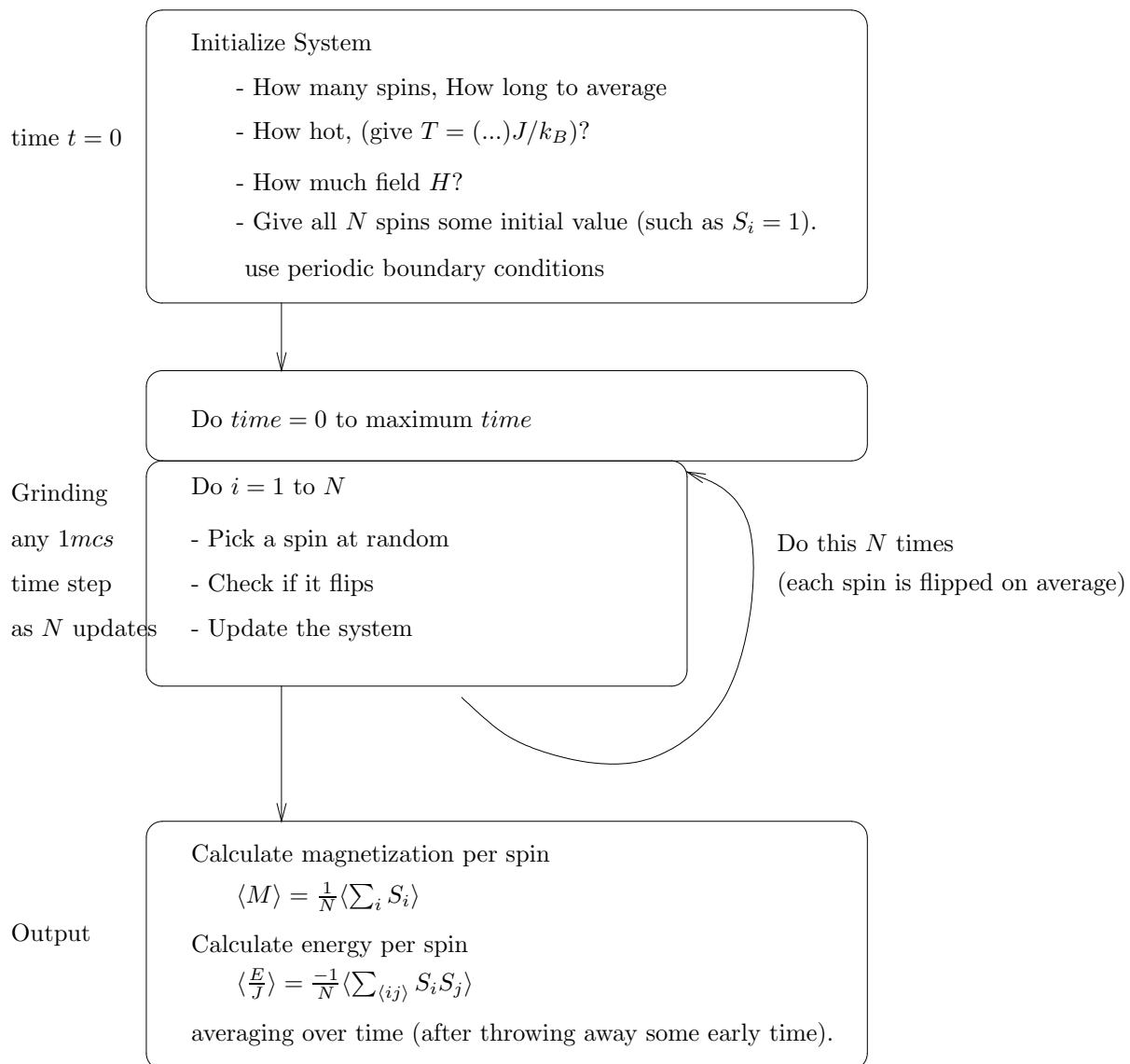
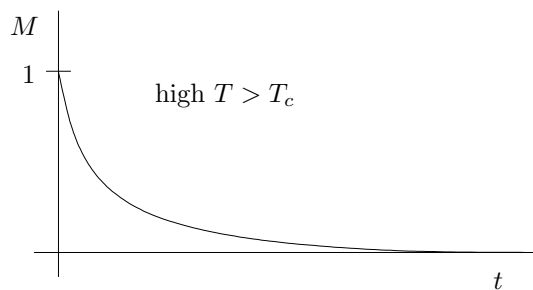


Figure 6.6:



t in Monte Carlo step 1, 1 unit of time
corresponds to attempting N spin flips

Figure 6.7:

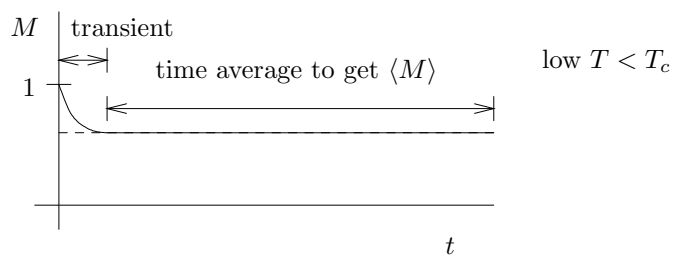


Figure 6.8:

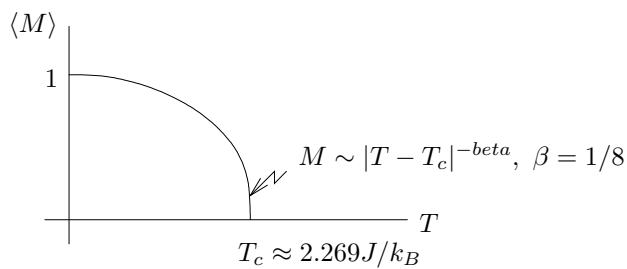


Figure 6.9:

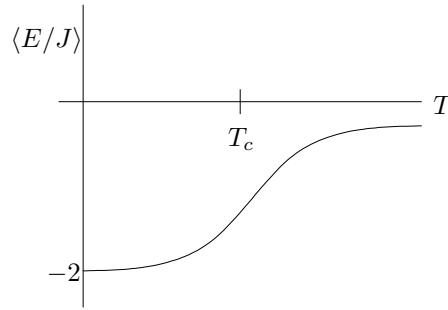


Figure 6.10:

initially $S_i = 1$, the magnetization quickly relaxes to zero (see fig. 6.7). Below T_c , the magnetization quickly relaxes to its equilibrium value (see fig. 6.8). Doing this for many temperatures, for a large enough lattice gives fig. 6.9. Doing this for the energy per spin gives fig. 6.10. which is pretty boring until one plots the heat capacity per spin

$$C \equiv \frac{1}{J} \frac{\partial \langle E \rangle}{\partial T}$$

Try it. You'll get very close to Ousager's results with fairly small systems

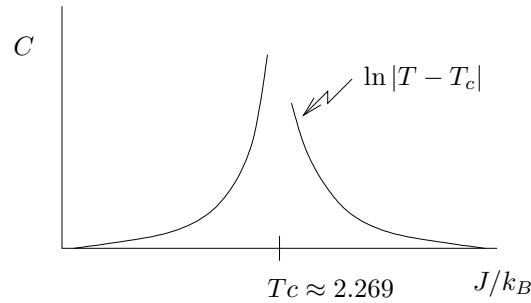


Figure 6.11:

$N = 10 \times 10$, or 100×100 over a thousand or so time steps, and you'll do much better than the mean field theory we did in class.

As an exercise, think how would you do this for the solid-on-solid model

$$Z = \sum_{\{\text{States}\}} e^{-E_{\text{State}}/k_B T}$$

where

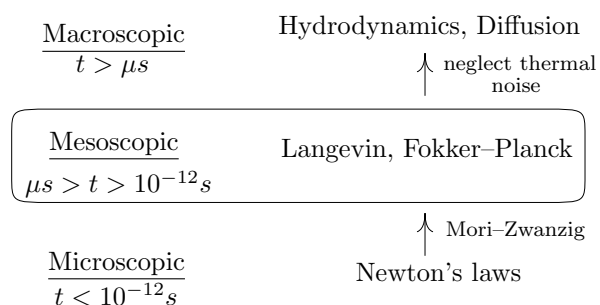
$$E_{\text{State}} = J \sum_{i=1}^N |h_i - h_{i+1}|$$

where h_i are heights at sites i .

Chapter 5

Nonequilibrium Theory Primer

How to go from microscopic to macroscopic? What is the most useful (mesoscopic) description?



5.1 Brownian Motion and L-R Circuits

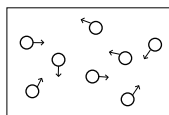


Figure 5.1: $1mu$ particles (balls) in fluid execute random looking path

Just looking in one dimension, $d = 1$

$$\langle x^2 \rangle \propto t \tag{5.1}$$

From which one can experimentally extract a diffusion constant

$$D \equiv \frac{\langle x^2 \rangle}{2t} \tag{5.2}$$

What is the equation of motion for a ball in a fluid?

$$m \frac{dv}{dt} = \text{Force} \quad (5.3)$$

Newton's law. And the force is a drag due to the fluid viscosity

$$\text{Force} = -\alpha v \quad (5.4)$$

where

$$\alpha = 6\pi\eta a \quad (5.5)$$

η is the viscosity, a the ball radius. Hence

$$\frac{dv}{dt} = -\alpha v \quad (5.6)$$

(where I will let $m = 1$ to simplify writing). This can be interpreted as a “hydrodynamic-like” equation for transport. In fact it is derived from the hydrodynamic equations, but I mean that it is a macroscopic description of a nonequilibrium — that is a transport — process.

It is unlike most dynamical equations that one sees for mechanics or in microphysics because it breaks time-reversal. Remember that $v \rightarrow -v$ under $t \rightarrow -t$, so Eq. 5.6 is not invariant under time reversal. Its solution is

$$v(t) = v_o e^{-\alpha t} \quad (5.7)$$

for some initial condition v_o . Note that any initial bump in v just decays away as shown in Fig. 5.2. This

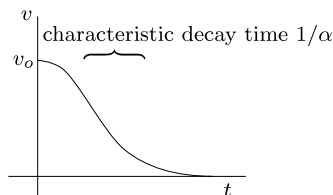


Figure 5.2:

has something to do with entropy increasing, but that's another story.

So how does time reversal get broken in Eq. 5.6 (or equivalently in hydrodynamics). There are a very large number of independent variables in the ball and fluid $\sim 10^{23}$. Most of these are of no consequence to the motion of a ball, and they have very fast characteristic relaxation times $\sim 10^{-10}$ seconds, which is the time for a sound wave to get scattered. In an experiment (or if one just watches) over the course of a second or a fraction of a second, one averages over something like 10^{10} of these very fast times. In theory, one ensemble averages the effects of “fast” variables to obtain the result on a “slow” variable like v . There is a large literature in this but its very involved.

Instead, let us simply look at the most simple correction to Eq. 5.6, in the spirit of the theory of thermodynamic fluctuations. Recall that there one finds that the corrections to thermodynamics satisfy relations like

$$\langle (\Delta T)^2 \rangle = \frac{k_B T^2}{C_v} \quad (5.8)$$

so that C_v , which is not calculated in thermodynamics, is given in terms of the temperature correlation function, for which one needs statistical mechanics. This is called a correlation–response relation or fluctuation–dissipation relation of the first kind. Following Langevin we say that the ball in the fluid is knocked around by the fluid particles (the other 10^{23} variables). Hence, instead of the macroscopic Eq. 5.6 we have the microscopic (or sometimes called mesoscopic) equation of motion.

$$\frac{dv}{dt} = -\alpha v + f(t) \quad (5.9)$$

The properties of $f(t)$, a random force, must be

$$\langle f(t) \rangle = 0 \quad (5.10)$$

And only the second moment is nontrivial (by the central-limit theorem, all higher-order moments are Gaussian, such as

$$\begin{aligned} \langle f(t_1)f(t_2)f(t_3)f(t_4) \rangle &= \langle f(t_1)f(t_2) \rangle \langle f(t_3)f(t_4) \rangle \\ &\quad + \langle f(t_1)f(t_3) \rangle \langle f(t_2)f(t_4) \rangle \\ &\quad + \langle f(t_1)f(t_4) \rangle \langle f(t_2)f(t_3) \rangle \end{aligned}$$

or essentially

$$\langle f^4 \rangle = 3 \langle f^2 \rangle^2$$

Since correlation of the f degrees of freedom decay in 10^{-10} seconds, we make the approximation, which is like taking the thermodynamic limit in equilibrium, that they decay instantaneously. That is

$$\langle f(t)f(t') \rangle = k_B T \Gamma \delta(t - t') \quad (5.11)$$

where Γ gives the strength of the noise (the $2k_B T$ is for convenience). (Note $\Gamma > 0$).

That is all there is to it, now we can solve the whole thing, and relate Γ to α , and obtain a fluctuation dissipation relation of the second kind. The solution of Eq. 5.9 (if $v_o = 0$ for convenience) is

$$v(t) = e^{-\alpha t} \int_0^t dt' e^{\alpha t'} f(t') \quad (5.12)$$

So if f is Gaussian, so is v . First we have

$$\langle v(t) \rangle = 0 \quad (5.13)$$

Now consider

$$\begin{aligned} \langle v(t)^2 \rangle &= e^{-2\alpha t} \int_0^t dt' \int_0^t dt'' e^{\alpha(t'+t'')} \langle f(t')f(t'') \rangle \\ &= 2k_B T \Gamma e^{-2\alpha t} \int_0^t dt' e^{2\alpha t'} \end{aligned}$$

thanks to the physicist's friend, the Dirac delta function. Hence

$$\langle v^2(t) \rangle = k_B T \left(\frac{\Gamma}{\alpha} \right) (1 - e^{-2\alpha t}) \quad (5.14)$$

But equipartition says that in equilibrium (presumably reached as $t \rightarrow \infty$),

$$\frac{1}{2}m\langle v^2 \rangle = \frac{1}{2}k_B T$$

so

$$\langle v^2(t = \infty) \rangle = k_B T \quad (5.15)$$

and we have the Einstein relation (implying $\alpha > 0$).

$$\underbrace{\alpha}_{\text{macroscopic}} = \underbrace{\Gamma}_{\text{microscopic}} \quad (5.16)$$

and the second fluctuation–dissipation relation:

$$\langle f(t)f(t') \rangle = 2k_B T \alpha \delta(t - t') \quad (5.17)$$

Compare this to Eq. 5.8 and think. It is easy to calculate other things, and here is one useful one:

$$\langle v(t')v(t' + t) \rangle = \langle v(0)v(t) \rangle = k_B T e^{-\alpha|t|} \quad (5.18)$$

For example, let's say one wants $\langle x^2(t) \rangle$, note that

$$x(t) = \int_0^t dt' v(t')$$

so that

$$\begin{aligned} \langle x^2(t) \rangle &= \int_0^t dt' \int_0^t dt'' \langle v(t')v(t'') \rangle \\ &= \int_0^t dt' \int_0^t dt'' \langle v(0)v(t'' - t') \rangle \end{aligned} \quad (5.19)$$

this takes a little fiddling. Let

$$\tau = t'' - t', \quad \bar{t} = \frac{1}{2}(t' + t'')$$

so that the Jacobian is unity and

$$t' = \bar{t} - \frac{\tau}{2}, \quad t'' = \bar{t} + \frac{\tau}{2}$$

The domain of integration is the box sketched in Fig. 5.3, so

$$\langle x^2(t) \rangle = \left[\int_{-t}^0 d\tau \int_{t''=0}^{t'=t} d\bar{t} + \int_0^t d\tau \int_{t'=0}^{t''=t} d\bar{t} \right] \langle v(0)v(\tau) \rangle$$

or,

$$\langle x^2(t) \rangle = \left[\int_{-t}^0 d\tau \int_{-\frac{\tau}{2}}^{t+\frac{\tau}{2}} d\bar{t} + \int_0^t d\tau \int_{\frac{\tau}{2}}^{t-\frac{\tau}{2}} d\bar{t} \right] \langle v(0)v(\tau) \rangle$$

The integrals are equal, and the \bar{t} integral can be done to give

$$\langle x^2(t) \rangle = 2 \int_0^t (t - t') \langle v(0)v(t') \rangle dt' \quad (5.20)$$

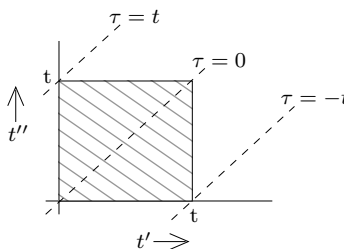


Figure 5.3:

From Eq. 5.18 one has

$$\begin{aligned}\langle x^2(t) \rangle &= 2k_B T t \int_0^t \left(1 - \frac{t'}{t}\right) e^{-\alpha t'} dt' \\ &\approx 2 \left(\frac{k_B T}{\alpha} \right) t + \dots \text{ (for late } t\text{)}\end{aligned}\tag{5.21}$$

(Do it more carefully if you want. Try $\langle x(t)x(t') \rangle$ too, if you want.) This is the form for one-dimensional diffusion, with the diffusion constant

$$D = \frac{k_B T}{\alpha}\tag{5.22}$$

This was used in the early 20TH century to estimate k_B , and hence Avagadro's number from the gas constant R .

$$\frac{R}{k_B} = 6.02 \times 10^{23}$$

The content is the same as Eqs. 5.16 and 5.17, but its more physical. This helped establish that liquids were composed of many particles at that time.

The same aproach can be used for noise in electrical circuits, called Johnson noise. If the current changes

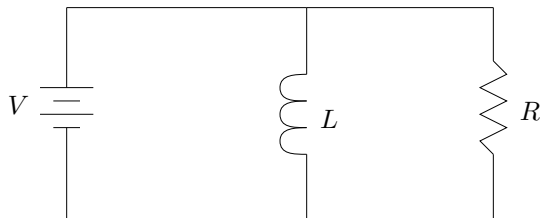


Figure 5.4:

di/dt with time the voltage resists it by $V = iR$ in

$$L \frac{di}{dt} = -Ri\tag{5.23}$$

where $L \equiv 1$ is inductance, R is resistance and i is current. Using unit inductance, and adding a random voltage:

$$\frac{di}{dt} = -Ri + f(t) \quad (5.24)$$

where R plays the role of transport coefficient and $\langle f \rangle = 0$

$$\langle f(t)f(t') \rangle = 2k_B T \Gamma \delta(t - t') \quad (5.25)$$

as before. As above

$$\langle i^2(t) \rangle = k_B T \left(\frac{\Gamma}{R} \right) (1 - e^{-2Rt}) \quad (5.26)$$

But the energy in an inductor is

$$Energy = \frac{1}{2} Li^2 \equiv \frac{1}{2} i^2$$

So by equipartition

$$\langle i^2 \rangle = k_B T$$

in equilibrium as $t \rightarrow \infty$ and hence:

$$\Gamma = R \quad (5.27)$$

the Nyquist theorem for the intensity of Johnson noise. Again, $R > 0$ implied.

5.2 Fokker–Planck Equation

These are both special (linear) cases. Now we will do a more general case. Say we have the Langevin equation

$$\frac{\partial m(t)}{\partial t} = v(m) + f(t) \quad (5.28)$$

where

$$\langle f(t)f(t') \rangle = 2k_B T \Gamma \delta(t - t')$$

(It is straightforward to generalize this to $m_i(t)$ or $m(\vec{r}, t)$, where $\langle f_i f_j \rangle \sim \delta_{ij} \delta(t - t')$, and $\langle f(\vec{r}) f(\vec{r}') \rangle \sim \delta(\vec{r} - \vec{r}') \delta(t - t')$).

We shall turn this into an equation for the probability distribution, called the Fokker–Planck equation, and derive a more sophisticated version of the fluctuation–dissipation theorem, (namely, $v(m) = -\Gamma \frac{\partial F}{\partial m}$, where F is a free energy).

Say M is the solution of the Langevin equation for some particular history of m being kicked around by the random force f . Clearly, the normalized probability distribution is the micro canonical

$$\rho(M, t) = \delta(M - m(t)) \quad (5.29)$$

Now let's be tricky by taking a time derivative

$$\frac{\partial \rho}{\partial t} = \dot{\rho} = -\dot{m} \frac{\partial}{\partial M} \delta(M - m(t))$$

or,

$$\dot{\rho} = \frac{\partial}{\partial M} (\dot{m}|_{m=M} \rho(M, t))$$

The formal solution of this is

$$\rho(M, t) = \left[e^{-\int_0^t dt' \frac{\partial}{\partial M} \dot{m}(t')|_{m=M}} \right] \rho(M, 0) \quad (5.30)$$

Now let us get the complete distribution by averaging over all histories of random forcings:

$$P(M, t) = \langle \rho(M, t) \rangle \quad (5.31)$$

and of course $P(M, 0) = \rho(M, 0)$. Hence,

$$P(M, t) = \langle e^{-\int_0^t dt' \frac{\partial}{\partial M} \dot{m}(t')|_{m=M}} \rangle P(M, 0)$$

or, recalling the Langevin equation 5.28:

$$P(M, t) = e^{-\int_0^t dt' \frac{\partial}{\partial M} v(M)} \langle e^{-\int_0^t dt' \frac{\partial}{\partial M} f(t')} \rangle P(M, 0)$$

But if a variable u is Gaussian, with $\langle u^2 \rangle = \sigma^2$, then $\langle e^u \rangle = e^{\sigma^2/2}$, and here we have

$$\langle f(t)f(t') \rangle = 2k_B T \Gamma \delta(t - t')$$

so

$$\langle e^{-\int_0^t dt' \frac{\partial}{\partial M} f(t')} \rangle = e^{k_B T \Gamma t \frac{\partial^2}{\partial M^2}}$$

and

$$P(M, t) = e^{t \frac{\partial}{\partial M} [-v + k_B T \Gamma \frac{\partial}{\partial M}]} P(M, 0)$$

or,

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial M} \left(-v(M) + k_B T \Gamma \frac{\partial}{\partial M} \right) P(M, t) \quad (5.32)$$

which is almost the Fokker-Planck equation. Note that the equilibrium solution, when $\partial P_{eq}/\partial t = 0$, is

$$v(M) = k_B T \Gamma \frac{\partial}{\partial M} \ln P_{eq}(M) \quad (5.33)$$

But

$$P_{eq}(M) = e^{-F(M)/k_B T} \quad (5.34)$$

Hence we must have

$$v(M) = -\Gamma \frac{\partial F}{\partial M} \quad (5.35)$$

which is, again, the fluctuation-dissipation relation. In summary, we have shown the equivalence of the Langevin equation

$$\frac{\partial m}{\partial t} = -\Gamma \frac{\partial F}{\partial m} + f \quad (5.36)$$

where f is a Gaussian random noise with

$$\langle f(t)f(t') \rangle = 2k_B T \Gamma \delta(t - t') \quad (5.37)$$

and the Fokker-Planck equation

$$\frac{\partial P}{\partial t} = \Gamma \frac{\partial}{\partial M} \left(\frac{\partial F}{\partial M} + k_B T \frac{\partial}{\partial M} \right) P(M, t) \quad (5.38)$$

with the equilibrium distribution

$$P_{eq} \propto e^{-F(M)/k_B T} \quad (5.39)$$

Next stop will be to show the limit in which the Master equation is equivalent to either the Fokker-Planck equation, or the Langevin equation.

5.3 Appendix 1

For brownian motion

$$m \frac{\partial v}{\partial t} = -\alpha v + f$$

$$\langle f(t)f(t') \rangle = 2k_B T m \alpha \delta(t - t')$$

with

$$\alpha = 6\pi\eta a = 2 \times 10^{-2} gm/sec \left\{ \begin{array}{l} \eta = 10^{-2} \overbrace{poise}^{\frac{gm}{cm \cdot sec}} \text{ (for water)} \\ a = 10^{-1} cm \\ m = \frac{1gm}{cm^3} \times \frac{4\pi}{3} (10^{-1})^3 \\ \quad = 4 \times 10^{-3} g \end{array} \right.$$

$$\frac{\alpha}{m} = \frac{5}{sec} = \frac{1}{\tau_{micro}}; \tau_{micro} \sim 0.2sec$$

which is macroscopic. Forcing a length by $l \equiv \frac{m}{\alpha} \sqrt{\frac{k_B T}{m}} \sim 200 \text{\AA}$, which is almost microscopic.

What are the properties of a random noise

$$\frac{dx}{dt} = \underbrace{F}_{deterministic} + \underbrace{f}_{random}$$

Do time averages over an interval $t \leq t_{macro}$. Say noise is only correlated for times $\sim t_{micro}$, where

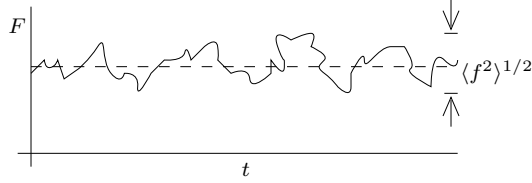


Figure 5.5: Cartoon, F should be a single valued function of t .

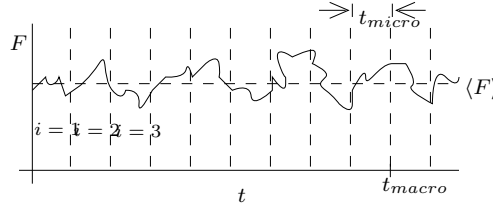
$t_{macro} \sim \text{seconds}$ and $t_{micro} \sim 10^{-10} \text{seconds}$. Or consider the hydrodynamic limit, or Markov process where,

$$\frac{t_{macro}}{t_{micro}} \rightarrow \infty \quad (5.40)$$

which is the analog of the thermodynamic limit. Here we take it by $t_{micro} \rightarrow 0$. It is by this limit that time reversal symmetry is broken and entropy increases. Call

$$N = \frac{t_{macro}}{t_{micro}} \quad (5.41)$$

the number of independent parts.

Figure 5.6: Cartoon, F should be a single valued function of t .

Hence

$$\langle F \rangle = \frac{1}{N} \sum_{i=1}^N \langle F_i \rangle = \mathcal{O}(1) \quad (5.42)$$

since the boxes are independent, and $\langle F_i \rangle$ knows nothing about the boxes. Similarly, the total for the random noise (over the t_{macro} time interval)

$$f^2 = \sum_i f_i \sum_j f_j$$

So its average is

$$\begin{aligned} \langle f^2 \rangle &= \frac{1}{N^2} \sum_j \langle f_i f_j \rangle \\ &= \frac{1}{N} \sum_i \langle f_i^2 \rangle + \text{uncorrelated} \\ &= \mathcal{O}\left(\frac{1}{N}\right) \end{aligned}$$

If we consider $1/N$ the result from averaging over some macroscopically short time interval, then

$$\langle f(t)f(t') \rangle = (\text{Const.})\delta(t-t')$$

gives the appropriate result for *any* macroscopically short time interval, regardless of how short (i.e. as $t_{micro} \rightarrow 0$). For convenience this gives Γ as

$$\langle f(t)f(t') \rangle = 2k_B T \Gamma \delta(t-t')$$

All higher moments are Gaussian by similar arguments.

5.4 Master Equation and Fokker-Planck Equation

Master Equation:

$$\frac{\partial P(s)}{\partial t} = \sum_{s'} \left[\underbrace{w(s, s')P(s')}_{\substack{s' \rightarrow s \\ \text{Fluctuations from} \\ \text{other states to } s}} - \underbrace{w(s, s')P(s)}_{\substack{s \rightarrow s' \\ \text{Fluctuations} \\ \text{out of } s}} \right] \quad (5.43)$$

In equilibrium

$$\frac{\partial P_{eq}}{\partial t} = 0 \quad (5.44)$$

where

$$P_{eq}(s) = e^{-E(s)} \quad (5.45)$$

(in units of temperature), so

$$w(s, s')e^{-E(s')} = w(s', s)e^{-E(s)} \quad (5.46)$$

which is the condition of detailed balance of fluctuations. One choice which satisfies this is due to Metropolis

$$W_{Metropolis}(s, s') = \begin{cases} e^{-\Delta E(s, s')} & , \quad \Delta E_s \\ 1 & , \quad \Delta E_{s'} \end{cases} \quad (5.47)$$

where $\Delta E(s, s') = E(s) - E(s')$. But the choice is somewhat arbitrary. For example, if we let

$$w(s, s') = D(s, s')e^{\frac{1}{2}(E(s') - E(s))} \quad (5.48)$$

then detailed balance is satisfied provided

$$D(s, s') = D(s', s) \quad (5.49)$$

With this transformation the particular Metropolis choice (Eq. 5.47) becomes:

$$D_{Metropolis}(s, s') = e^{-\frac{1}{2}|\Delta E(s, s')|} \quad (5.50)$$

Note that *all* the equilibrium statistical mechanics is satisfied by Eq. 5.49 however.

Hence, Eq. 5.43 becomes:

$$\frac{\partial P(s)}{\partial t} = \sum_{s'} D(s, s') \left[e^{\frac{1}{2}(E(s') - E(s))} P(s') - e^{-\frac{1}{2}(E(s') - E(s))} P(s) \right] \quad (5.51)$$

where D is only due to transport.

Now we will derive the Fokker-Planck equation.

Most fluctuations involve nearby states s and s' . So we can expand the transport matrix as (Kramers-Moyal expansion)

$$D(s, s') = D_o \delta_{s, s'} + D_2 \frac{\partial^2}{\partial (s - s')^2} \delta_{s, s'} + \dots \quad (5.52)$$

Odd terms cannot appear since $D(s, s') = D(s', s)$ and we are evidently writing $D(s, s') = f(s - s')$.

The first term, $D_o \delta_{s, s'}$, gives no contribution to Eq. 5.51. So we consider the first nontrivial term

$$D(s, s') = D_2 \frac{\partial^2}{\partial s^2} \delta_{s, s'} \quad (5.53)$$

Note $\frac{\partial^2}{\partial (s - s')^2}$ has the same action on $\delta_{s, s'}$ as $\partial^2 / \partial s^2$.

$$\frac{\partial P(s)}{\partial t} = D_2 \sum_{s'} \left(\frac{\partial^2}{\partial s^2} \delta_{s, s'} \right) \left[e^{-\frac{1}{2}\Delta E} P(s') - e^{\frac{1}{2}\Delta E} P(s) \right] \quad (5.54)$$

or, on simplifying

$$\frac{\partial P(s)}{\partial t} = D_2 e^{-\frac{E(s)}{2}} \frac{\partial^2}{\partial s^2} \sum_{s'} \delta_{s,s'} e^{\frac{E(s')}{2}} P(s') - D_2 e^{\frac{E(s)}{2}} P(s) \frac{\partial^2}{\partial s^2} \sum_{s'} \delta_{s,s'} e^{-\frac{E(s)}{2}}$$

or,

$$\frac{\partial P}{\partial t} = D_2 e^{-\frac{E(s)}{2}} \frac{\partial^2}{\partial s^2} \left(e^{\frac{E(s)}{2}} P(s) \right) - D_2 e^{\frac{E(s)}{2}} P(s) \frac{\partial^2}{\partial s^2} \left(e^{-\frac{E(s)}{2}} \right) \quad (5.55)$$

Now consider

$$\frac{\partial}{\partial s} e^{\frac{E(s)}{2}} p(s) = \frac{1}{2} \frac{\partial E}{\partial s} e^{\frac{E}{2}} P + e^{\frac{E}{2}} \frac{\partial P}{\partial s}$$

and

$$\frac{\partial}{\partial s} e^{-\frac{E}{2}} = -\frac{1}{2} \frac{\partial E}{\partial s} e^{-\frac{E}{2}} \quad (5.56)$$

so

$$\frac{\partial^2}{\partial s^2} \left(e^{\frac{E}{2}} P \right) = \frac{1}{2} \frac{\partial^2 E}{\partial s^2} e^{\frac{E}{2}} P + \frac{1}{4} \left(\frac{\partial E}{\partial s} \right)^2 e^{\frac{E}{2}} P + \frac{2}{2} \frac{\partial E}{\partial s} e^{\frac{E}{2}} \frac{\partial P}{\partial s} + e^{\frac{E}{2}} \frac{\partial^2 P}{\partial s^2} \quad (5.57)$$

or

$$e^{-\frac{E}{2}} \frac{\partial^2}{\partial s^2} \left(e^{\frac{E}{2}} P \right) = \frac{1}{2} \frac{\partial^2 E}{\partial s^2} P + \frac{1}{4} \left(\frac{\partial E}{\partial s} \right)^2 P + \frac{\partial E}{\partial s} \frac{\partial P}{\partial s} + \frac{\partial^2 P}{\partial s^2} \quad (5.58)$$

and from Eq. 5.56

$$\frac{\partial^2}{\partial s^2} e^{-E/2} = -\frac{1}{2} \frac{\partial^2 E}{\partial s^2} e^{-\frac{E}{2}} + \frac{1}{4} \left(\frac{\partial E}{\partial s} \right)^2 e^{-\frac{E}{2}} \quad (5.59)$$

or,

$$e^{E/2} P \frac{\partial^2}{\partial s^2} e^{-E/2} = -\frac{1}{2} \frac{\partial^2 E}{\partial s^2} P + \frac{1}{4} \left(\frac{\partial E}{\partial s} \right)^2 P \quad (5.60)$$

Using Eq. 5.58 and Eq. 5.60 in Eq. 5.55 (just subtract them):

$$\frac{\partial P}{\partial t} = D_2 \left[\frac{\partial^2 E}{\partial s^2} P + \frac{\partial E}{\partial s} \frac{\partial P}{\partial s} + \frac{\partial^2 P}{\partial s^2} \right]$$

Note how the 1/2 factor disappears, or,

$$\frac{\partial P}{\partial t} = D_2 \frac{\partial}{\partial s} \left[\frac{\partial E}{\partial s} + \frac{\partial}{\partial s} \right] P \quad (5.61)$$

called the Fokker-Planck equation. To check its consistancy with equilibrium, note

$$\frac{\partial P_{eq}}{\partial t} = 0$$

or

$$\left[\frac{\partial E}{\partial s} + \frac{\partial}{\partial s} \right] P_{eq} = 0$$

$$\frac{\partial E}{\partial s} = -\frac{\partial \ln P_{eq}}{\partial s}$$

or

$$P_{eq} \propto e^{-E} \quad (5.62)$$

as it should.

Evidently the Fokker–Planck equation can be rewritten as

$$\frac{\partial P(s)}{\partial t} = \sum_{s'} L_{FP}(s, s') P(s') \quad (5.63)$$

where

$$L_{FP}(s, s') = D_2 \frac{\partial}{\partial s} \left[\frac{\partial E}{\partial s} + \frac{\partial}{\partial s} \right] \delta_{s, s'} \quad (5.64)$$

We'll now return to the Master equation to give a similar form.

Consider Eq. 5.51. The second piece on the right-hand side is

$$Piece = \sum_{s'} D(s, s') \left[-e^{-\frac{1}{2}(E(s')-E(s))} P(s) \right] \quad (5.65)$$

The awkwardness is that $P(s)$ is not summed out. First let the dummy index s' be s'' , so

$$Piece = \sum_{s''} D(s, s'') \left[-e^{-\frac{1}{2}(E(s'')-E(s))} P(s) \right]$$

Now replace $P(s)$ by $\sum_{s'} \delta_{s, s'} P(s')$, giving

$$Piece = \sum_{s'} \left[- \left(\underbrace{\sum_{s''} D(s, s'') e^{-\frac{1}{2}(E(s'')-E(s))}}_{\text{some function of } s} \right) \delta_{s, s'} P(s) \right] \quad (5.66)$$

Now put this back into Eq. 5.51 to get

$$\frac{\partial P(s)}{\partial t} = \sum_{s'} \left\{ D(s, s') e^{\frac{1}{2}(E(s')-E(s))} P(s') - \left(\sum_{s''} D(s, s'') e^{-\frac{1}{2}(E(s'')-E(s))} \right) \delta_{s, s'} P(s') \right\} \quad (5.67)$$

or,

$$\frac{\partial P(s)}{\partial t} = \sum_{s'} L_{ME}(s, s') P(s') \quad (5.68)$$

where

$$L_{ME} = D(s, s') e^{\frac{1}{2}(E(s')-E(s))} - \left(\sum_{s''} D(s, s'') e^{-\frac{1}{2}(E(s'')-E(s))} \right) \delta_{s, s'} \quad (5.69)$$

Making the Kramers–Moyal approximation

$$D(s, s') \rightarrow D_2 \frac{\partial^2}{\partial s^2} \delta_{s, s'}$$

should recover

$$L_{ME}(s, s') \rightarrow L_{FP}(s, s')$$

Note there is still freedom to choose the symmetric matrix $D(s, s')$ in Eq. 5.69.

In either the Fokker-Planck equation (Eq. 5.63) or the Master equation (Eq. 5.68), we can introduce a transformation which makes $L(s, s')$ symmetric. Let

$$\Lambda \equiv e^{\frac{1}{2}E(s)} L(s, s') e^{-\frac{1}{2}E(s')} \quad (5.70)$$

Then in Eq. 5.69 we have

$$\Lambda_{ME}(s, s') = D(s, s') - \left[\sum_{s''} D(s, s'') e^{-\frac{1}{2}(E(s'') - E(s))} \right] \delta_{s, s'} \quad (5.71)$$

which is symmetric, since D is symmetric.

For the Fokker-Planck equation (Eq. 5.64)

$$\begin{aligned} \Lambda_{FP} &= D_2 e^{\frac{E(s)}{2}} \frac{\partial}{\partial s} \left[\frac{\partial E}{\partial s} + \frac{\partial}{\partial s} \right] \delta_{s, s'} e^{-E(s)/2} \\ &= D_2 \left[\frac{\partial^2 E}{\partial s^2} \delta_{s, s'} + \frac{\partial E}{\partial s} e^{E(s)/2} \frac{\partial}{\partial s} \left(e^{-E(s)/2} \delta_{s, s'} \right) + e^{E(s)/2} \frac{\partial^2}{\partial s^2} \delta_{s, s'} e^{-E(s)/2} \right] \end{aligned} \quad (5.72)$$

Now consider

$$\frac{\partial}{\partial s} \delta_{s, s'} e^{-E(s)/2} = -\frac{1}{2} \frac{\partial E}{\partial s} e^{-E(s)/2} \delta_{s, s'} + e^{-E(s)/2} \frac{\partial}{\partial s} \delta_{s, s'} \quad (5.73)$$

Taking one more derivative gives

$$\frac{\partial^2}{\partial s^2} \delta_{s, s'} e^{-E/2} = -\frac{1}{2} \frac{\partial^2 E}{\partial s^2} e^{-E/2} \delta_{s, s'} + \frac{1}{4} \left(\frac{\partial E}{\partial s} \right)^2 e^{-E/2} \delta_{s, s'} + e^{-E/2} \frac{\partial^2}{\partial s^2} \delta_{s, s'} \quad (5.74)$$

Using Eq. 5.73 and Eq. 5.74 in Eq. 5.72 gives

$$\Lambda_{FP}(s, s') = D_2 \left[\frac{1}{2} \frac{\partial^2 E}{\partial s^2} \delta_{s, s'} - \frac{1}{4} \left(\frac{\partial E}{\partial s} \right)^2 \delta_{s, s'} + \frac{\partial^2}{\partial s^2} \delta_{s, s'} \right] \quad (5.75)$$

so, letting

$$\rho(s) \equiv e^{\frac{E(s)}{2}} P(s) \quad (5.76)$$

we have

$$\frac{\partial \rho(s)}{\partial t} = \sum_{s'} \Lambda(s, s') \rho(s) \quad (5.77)$$

where

$$\Lambda(s, s') = \Lambda(s', s) \quad (5.78)$$

and

$$\Lambda_{ME}(s, s') = D(s, s') - \left[\sum_{s''} D(s, s'') e^{-\frac{1}{2}(E(s'') - E(s))} \right] \delta_{s, s'} \quad (5.79)$$

or if $D(s, s') = D_2 \frac{\partial^2}{\partial s^2} \delta_{s, s'}$,

$$\Lambda_{FP}(s, s') = D_2 \left[\frac{1}{2} \frac{\partial^2 E}{\partial s^2} - \frac{1}{4} \left(\frac{\partial E}{\partial s} \right)^2 + \frac{\partial^2}{\partial s^2} \right] \delta_{s, s'} \quad (5.80)$$

Note that detailed balance is satisfied by $D(s, s') = D(s', s)$. Also, the equilibrium distribution of $\rho(s)$ is

$$\rho_{eq}(s) \propto e^{-\frac{E(s)}{2}} \quad (5.81)$$

Normalization can be fixed by a multiplicative constant in Eq. 5.76.

The formal solution of Eq. 5.77 is

$$\rho(s, t) = \sum_{s'} e^{\Lambda(s, s')t} \rho(s', 0) \quad (5.82)$$

Since $\Lambda(s, s')$ is symmetric, it has real eigenvalues denoted by $(-1/\tau_s)$ say, i.e.

$$\rho(s, t) = \sum_{s'} e^{-t/\tau_{s'}} \rho(s', 0) \quad (5.83)$$

The largest of these, τ say, should often satisfy

$$\tau(N) = N^{z/d} \quad (5.84)$$

where d is the dimension of space of a system with N constituents, and z is an exponent for slowing down.

Let us return now to the dependence of $D(s, s')$. As mentioned before, detailed balance is satisfied by requiring this to be a symmetric matrix. Furthermore, we obtained the Fokker–Planck equation by expanding it. That is

$$D(s, s') = D(s', s)$$

and

$$D(s, s') \approx D_0 \delta_{s, s'} + D_2 \frac{\partial^2}{\partial s^2} \delta_{s, s'}$$

are our only conditions on D , and neither fix the temperature dependence — if any — of this quantity. In fact, we require no further dependence on temperature for consistency with equilibrium.

But let us consider the Metropolis and Glauber choices for transition probabilities. Eq. 5.47

$$W_{Metropolis} = \begin{cases} e^{-\Delta E(s, s')}, & \Delta E > c \\ 1, & \Delta E \leq c \end{cases}$$

and

$$W_{Glauber} = \frac{1}{2} \left(1 - \tanh \frac{\Delta E(s, s')}{2} \right) \quad (5.85)$$

which both satisfy detailed balance, and give, Eq. 5.50

$$D_{Metropolis} = e^{-\frac{1}{2}|\Delta E|}$$

and

$$D_{Glauber} = \frac{1}{2 \cosh \Delta E} \quad (5.86)$$

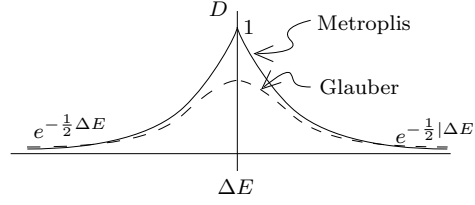


Figure 5.7:

which are symmetric, but with strong dependences on temperature and the Hamiltonian.

Evidently they are of this form, at least partly, so that $W \leq 1$. Note that, if $W = 1$, $D = e^{-\frac{1}{2}\Delta E}$, so that the largest D can be is bounded by the Metropolis rule (Eq. 5.50), shown in Fig. 5.7.

Hence any rule sitting “under” the Metropolis rule is valid, e.g. Fig. 5.8 or Fig. 5.9. The second of these, or perhaps something else, may be useful for high-temperature series expansions, since

$$D_{\text{Metropolis}} \approx 1 - \mathcal{O}(|\Delta E|)$$

while

$$D_{\text{Glauber}} \approx \frac{1}{2} - \mathcal{O}((\Delta E)^2)$$

as $\Delta E \rightarrow 0$.

But now let’s consider the Fokker–Planck equation with the operator

$$D_{FP}(s, s') = D_o \delta_{s, s'} + D_2 \frac{\partial^2}{\partial s^2} \delta_{s, s'}$$

Note D is now negative close to $\Delta E = 0$.

This seems at odds with interpreting

$$w = D e^{\frac{1}{2}\Delta E}$$

as a probability on $0 \rightarrow 1$, (up to a trivial rate constant).

Perhaps one should consider a coarse-grained D_{FP} , which will give a positive definite D_{FP} (coarse-grain over a narrow Gaussian say).

In any case, it is interesting to note that if one chooses

$$D(s, s') = \bar{D}$$

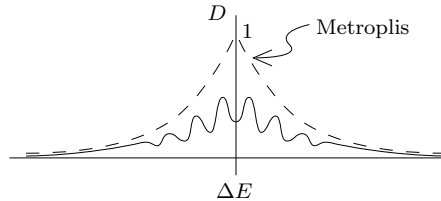


Figure 5.8:

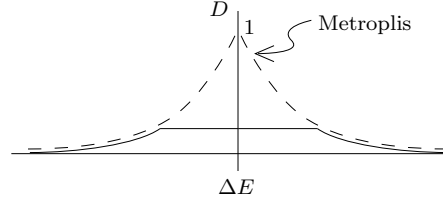


Figure 5.9:

a constant, and scales time in these units, that one has the symmetric Master equation from Eq. 5.77

$$\frac{\partial \rho(s)}{\partial t} = \sum_{s'} \Lambda(s, s') \rho(s')$$

with (Eq. 5.78):

$$\Lambda_{ME}(s, s') = 1 - \delta_{s,s'} \sum_{s''} e^{-\frac{1}{2}(E(s'') - E(s))}$$

This is fine for Ising models above a temperature T_o where

$$e^{\frac{1}{2}\Delta E(s, s', T_o)} \equiv \bar{D}$$

This looks “not too bad” since $\sum_{s''} e^{-\frac{1}{2}E(s'')} = Z(2T)$ giving

$$\Lambda_{ME}(s, s') = 1 - \delta_{s,s'} e^{\frac{1}{2}E(s)} Z$$

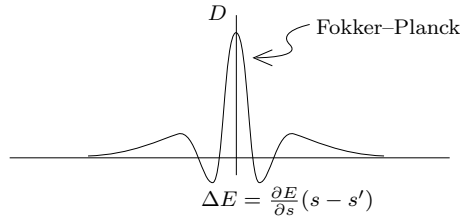


Figure 5.10:

5.5 Appendix 2: H theorem for Master Equation

For convenience let $T = 1$ (that is measure energy in units of temperature). The free energy

$$F = E - TS$$

becomes

$$F = E - S \tag{5.87}$$

which, in thermodynamics, is minimized in equilibrium. We will show that

$$\frac{\partial F}{\partial t} \leq 0 \quad (5.88)$$

from the Master equation, where

$$F = \langle E \rangle - \langle -\ln P \rangle$$

Then

$$F = \sum_s E_s P_s + \sum_s P_s \ln P_s \quad (5.89)$$

so,

$$\frac{dF}{dt} = \sum_s E_s \frac{dP_s}{dt} + \sum_s \frac{dP_s}{dt} \ln P_s + \sum_s \cancel{\frac{dP_s}{dt}} \overset{0}{\phantom{\frac{dP_s}{dt}}} \quad (5.90)$$

Using $\sum_s P_s = 1$ so that

$$\frac{d}{dt} \left(\sum_s P_s \right) = \frac{d}{dt} 1 = 0 \quad (5.91)$$

Hence

$$\frac{dF}{dt} = \sum_s (E_s + \ln P_s) \frac{P_s}{dt} \quad (5.92)$$

But, from Eq. 5.51

$$\frac{dP_s}{dt} = \sum_{s'} D_{s,s'} \left\{ e^{-\frac{1}{2}\Delta E_{s,s'}} P_{s'} - e^{\frac{1}{2}\Delta E_{s,s'}} P_s \right\} \quad (5.93)$$

is the Master equation, where

$$\Delta E_{s,s'} \equiv E_s - E_{s'} \quad (5.94)$$

$$D_{s,s'} = D_{s',s} \quad (5.95)$$

and

$$D_{s,s'} \geq 0 \quad (5.96)$$

Dropping all the subscripts gives

$$\frac{dF}{dt} = \sum_{s,s'} D \left\{ (E + \ln P) e^{-\frac{1}{2}\Delta E} P' - (E' + \ln P') e^{\frac{1}{2}\Delta E} P \right\} \quad (5.97)$$

Switching the (invisible) indices gives the equivalent equation,

$$\frac{dF}{dt} = \sum_{s,s'} D \left\{ (E' + \ln P') e^{\frac{1}{2}\Delta E} P - (E + \ln P) e^{-\frac{1}{2}\Delta E} P' \right\} \quad (5.98)$$

Adding these together, dividing by 2, gives the handy symmetric form

$$\frac{dF}{dt} = \sum_{s,s'} \frac{D}{2} \left\{ (E - E' + \ln P - \ln P') e^{-\frac{1}{2}\Delta E} P' - (E - E' + \ln P - \ln P') e^{\frac{1}{2}\Delta E} P \right\} \quad (5.99)$$

or,

$$\begin{aligned}
&= \sum_{s,s'} \frac{D}{2} \left\{ (\Delta E + \ln P - \ln P') (e^{-\frac{1}{2}\Delta E} P' - e^{\frac{1}{2}\Delta E} P) \right\} \\
&= \sum_{s,s'} \frac{D}{2} \left\{ \left[\ln P + \frac{\Delta E}{2} - \left(\ln P' - \frac{\Delta E}{2} \right) \right] \left[e^{-\frac{1}{2}\Delta E} P' - e^{\frac{1}{2}\Delta E} P \right] \right\} \\
\frac{dF}{dt} &= - \sum_{s,s'} \frac{D}{2} \left\{ \left[\ln(P' e^{-\frac{1}{2}\Delta E}) - \ln(P e^{\frac{1}{2}\Delta E}) \right] \left[e^{-\frac{1}{2}\Delta E} P' - e^{\frac{1}{2}\Delta E} P \right] \right\}
\end{aligned} \tag{5.100}$$

Note that the term in the curly brackets is of the form

$$\{....\} = (\ln x - \ln y)(x - y) \tag{5.101}$$

But if $\ln x > \ln y$, then $x > y$ so,

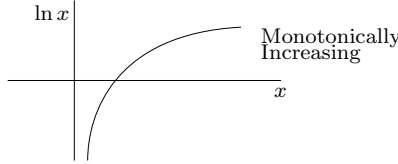


Figure 5.11:

$$(\ln x - \ln y)(x - y) \geq 0 \tag{5.102}$$

where the equality only applies for $x = y$. Hence, since $D > 0$ in Eq. 5.100 we have

$$\frac{dF}{dt} \leq 0 \tag{5.103}$$

which is the H theorem for the canonical ensemble. The equality holds if

$$P' e^{-\frac{1}{2}\Delta E} = P e^{\frac{1}{2}\Delta E}$$

i.e., for

$$P \propto e^{-E} \tag{5.104}$$

5.6 Appendix 3: Derivation of Master Equation

Write down a reasonable starting point for the dynamics of the probability P being in a state $s \equiv \{M_i\}$, where M_i is, say, an order parameter, and i denotes lattice positions.

As time goes on, the probability of being in state s *increases* because one makes transitions *into* this state from other states like s' with probability $W(s, s')$. It can be handy to read this as $W(s, s') = W(s \leftarrow s')$. Anyway,

$$W(s, s')P(s')$$

are contributions *increasing* $P(s)$.

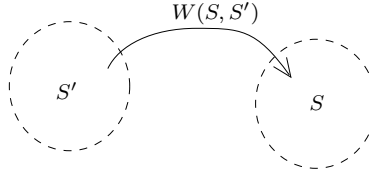


Figure 5.12:

However, $P(s)$ *decreases* because one makes transitions *out* of this state *into* states s' with probability $W(s', s) = W(s' \leftarrow s)$. Thus, $W(s', s)P(s)$ are contributions decreasing $P(s)$.

The Master equation is therefore

$$\frac{\partial P(s)}{\partial t} = \sum_{s'} \left[\underbrace{W(s, s')P(s')}_{s' \rightarrow s} - \underbrace{W(s', s)P(s)}_{s \rightarrow s'} \right]$$

which evidently breaks time reversal.

Note that $P(t)$ only depends on states infinitesimally close in time $P(t - dt)$. Thus, the Master equation considers a Markov process.

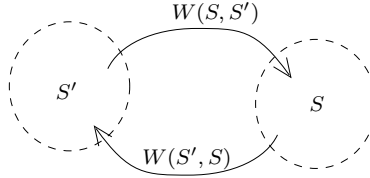


Figure 5.13:

5.7 Mori–Zwanzig Formalism

The fundamental equations of motion for particles of mass m interacting via a potential V are

$$\frac{\partial \vec{r}_i}{\partial t} = \frac{1}{m} \vec{\rho}_i$$

and

$$\frac{\partial \vec{\rho}_i}{\partial t} = -\frac{\partial}{\partial \vec{r}_i} \sum_{j=1}^N V(|\vec{r}_i - \vec{r}_j|) \quad (5.105)$$

in the classical limit, where $i = 1, 2, \dots, N$ are the N particles, with positions \vec{r}_i and momenta ρ_i . A run-of-the-mill potential has the form shown in Fig. 5.14 where $N \sim 10^{23}$. Hence there are 10^{23} coupled equations of motion with 10^{23} initial conditions.

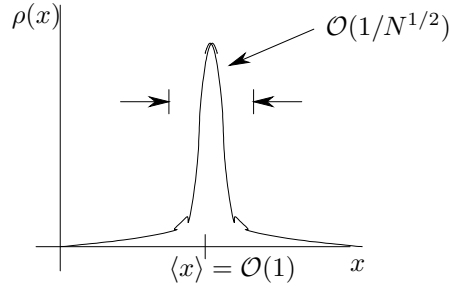


Figure 3.7: Gaussian (Width Exaggerated)

Which is to say again that fluctuations are small, and average values are well

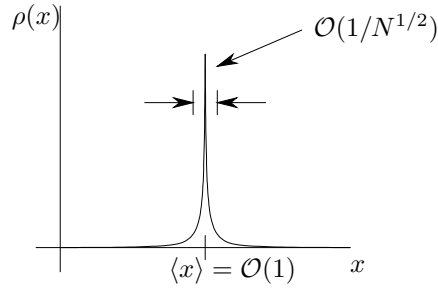


Figure 3.8: Gaussian (Width (sort of) to scale)

defined for a system of many ($N \rightarrow \infty$) independent parts.

3.3 Correlations in Space

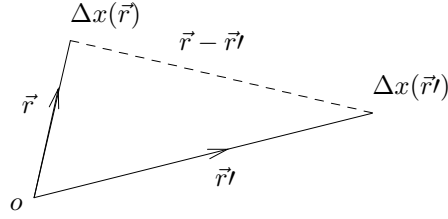
The results so far apply to a large system, and perhaps it is not surprising that the global fluctuations in a large system are small. These results for the global fluctuations have implications for the correlations of quantities, though. Say the intensive variable x has different values at points \vec{r} in space. (Precisely, let $d\vec{r}$, the volume element, be microscopically large, but macroscopically small). Consider the correlation function

$$\langle \Delta x(\vec{r}) \Delta x(\vec{r}') \rangle \equiv C(\vec{r}, \vec{r}') \quad (3.34)$$

We can say a few things about $C(\vec{r}, \vec{r}')$ from general considerations.

1. If space is translationally invariant, then the origin of the coordinate system for \vec{r} and \vec{r}' is arbitrary. It can be placed at point \vec{r} or \vec{r}' . The physical length of interest is $(\vec{r} - \vec{r}')$ or $(\vec{r}' - \vec{r})$. Hence

$$C(\vec{r}, \vec{r}') = C(\vec{r} - \vec{r}') = C(\vec{r}' - \vec{r}) \quad (3.35)$$

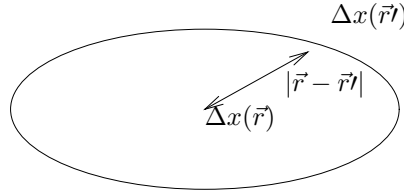
Figure 3.9: Translational invariance (only $\vec{r} - \vec{r}'$ is important)

and, of course,

$$\langle \Delta x(\vec{r}) \Delta x(\vec{r}') \rangle = \langle \Delta x(\vec{r} - \vec{r}') \Delta x(0) \rangle \quad (3.36)$$

etc.

2. If space is isotropic, then the direction of $\Delta x(\vec{r})$ from $\Delta x(\vec{r}')$ is unimportant, and only the magnitude of the distance $|\vec{r} - \vec{r}'|$ is physically

Figure 3.10: Isotropy (only $|\vec{r} - \vec{r}'|$ is important)

relevant. Hence

$$C(\vec{r}, \vec{r}') = C(|\vec{r} - \vec{r}'|) \quad (3.37)$$

So what was a function of 6 numbers (\vec{r}, \vec{r}') is now a function of only 1, $|\vec{r} - \vec{r}'|$.

3. Usually correlations fall off if points are arbitrarily far apart. That is,

$$\begin{aligned} \langle \Delta x(r \rightarrow \infty) \Delta x(0) \rangle &= \langle \Delta x(r \rightarrow \infty) \rangle \langle \Delta x(0) \rangle \\ &= 0 \end{aligned}$$

or

$$C(r \rightarrow \infty) = 0 \quad (3.38)$$

The scale of the correlation is set by the correlation length.

Now we know

$$C(|\vec{r} - \vec{r}'|) = \langle \Delta x(\vec{r}) \Delta x(\vec{r}') \rangle \quad (3.39)$$

Subject to these conditions. A constraint on $C(|\vec{r} - \vec{r}'|)$ is provided by our previous result

$$\langle (\Delta x)^2 \rangle = \mathcal{O}\left(\frac{1}{N}\right)$$

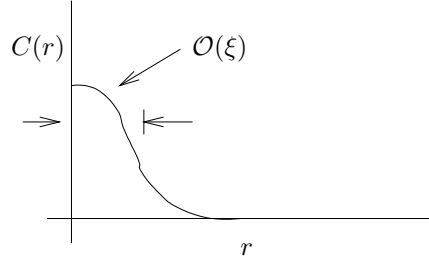


Figure 3.11: Typical correlation function

for a global fluctuation. Clearly,

$$\begin{aligned}\Delta x &= \frac{\int d\vec{r} \Delta x(\vec{r})}{\int d\vec{r}} \\ &= \frac{1}{V} \int d\vec{r} \Delta x(\vec{r})\end{aligned}\tag{3.40}$$

So we have

$$\begin{aligned}\frac{1}{V} \int d\vec{r} \int d\vec{r}' \langle \Delta x(\vec{r}) \Delta x(\vec{r}') \rangle &= \langle (\Delta x)^2 \rangle \\ &= \mathcal{O}\left(\frac{1}{N}\right)\end{aligned}\tag{3.41}$$

or,

$$\int d\vec{r} \int d\vec{r}' C(\vec{r} - \vec{r}') = \mathcal{O}\left(\frac{V^2}{N}\right)$$

Let $\vec{R} = \vec{r} - \vec{r}'$, $\vec{R}' = \frac{1}{2}(\vec{r} + \vec{r}')$. The Jacobian of the transformation is unity, and we obtain

$$\begin{aligned}\int d\vec{R}' \int d\vec{R} C(\vec{R}) &= \mathcal{O}\left(\frac{V^2}{N}\right) \\ &= V \int d\vec{R} C(\vec{R})\end{aligned}\tag{3.42}$$

So letting $\vec{R} \rightarrow \vec{r}$,

$$\int d\vec{r} C(\vec{r}) = \mathcal{O}\left(\frac{V}{N}\right)$$

But $N = \frac{V}{\xi^3}$, or in d dimensions, $N = \frac{L^d}{\xi^d}$, so

$$\int d\vec{r} C(\vec{r}) = \mathcal{O}(\xi^3)$$

or

$$\int d\vec{r} \langle \Delta x(\vec{r}) \Delta x(0) \rangle = \mathcal{O}(\xi^3)\tag{3.43}$$

for a system of $N \rightarrow \infty$ independant parts. This provides a constraint on correlations. It is a neat result in Fourier space. Let

$$\hat{C}(\vec{k}) \equiv \int d\vec{r} e^{i\vec{k} \cdot \vec{r}} C(\vec{r})$$

and finally

$$C(\vec{r}) = \int \frac{d\vec{k}}{(2\pi)^d} e^{-i\vec{k} \cdot \vec{r}} \hat{C}(\vec{k}) \quad (3.44)$$

and,

$$\langle |\Delta \hat{x}(k)|^2 \rangle \equiv \int d\vec{r} e^{i\vec{k} \cdot \vec{r}} \langle \Delta x(\vec{r}) \Delta x(0) \rangle$$

Hence the constraint of Eq. 3.43 is

$$\lim_{k \rightarrow 0} \hat{C}(k) = \mathcal{O}(\xi^3)$$

or

$$\lim_{k \rightarrow 0} \langle |\Delta \hat{x}(k)|^2 \rangle = \mathcal{O}(\xi^3) \quad (3.45)$$

Many functions satisfy the constraint of Eq. 3.43 (see Fig. 3.11). It turns out that usually,

$$\langle \Delta x(\vec{r}) \Delta x(0) \rangle \sim e^{-r/\xi} \quad (3.46)$$

for large r , which satisfies Eq. 3.43. This is obtained from analyticity of $(\hat{C}(k))^{-1}$ near $k = 0$. It can be argued,

$$\frac{1}{\hat{C}(k)} \approx (const.) + (const.)k^2 + \dots$$

so that $\langle |\Delta \hat{x}(k)|^2 \rangle = \frac{const.}{const. + k^2}$ near $k = 0$. Fourier transformation gives the result of Eq. 3.46 above.

(Note: In the previous notation with boxes, as in Fig. 3.4, we had

$$\Delta X = \sum_i \Delta X_i$$

or

$$\Delta x = \frac{1}{N} \sum_i \Delta X_i$$

This means

$$\frac{1}{V} \int d\vec{r} \Delta x(\vec{r}) = \frac{1}{N} \sum_i \Delta X_i \quad (3.47)$$

This is satisfied by

$$\Delta x(r) = \frac{V}{N} \sum_{i=1}^N \delta(\vec{r} - \vec{r}_i) \Delta X_i$$

where \vec{r}_i is a vector pointing to box i , and $\Delta X_i = \Delta X(\vec{r}_i)$.

Let me emphasize again that all these results follow from a system having $N \rightarrow \infty$ independent parts. To recapitulate, for $x = X/N$, where X is extensive, $N = V/\xi^3$ is the number of independent parts. V is the volume, and ξ is the correlation length:

$$\langle x \rangle = \mathcal{O}(1) \tag{3.7}$$

$$\langle (\Delta x)^2 \rangle = \mathcal{O}\left(\frac{1}{N}\right) \tag{3.15}$$

$$\rho(x) \propto e^{\frac{(x - \langle x \rangle)^2}{2\langle (\Delta x)^2 \rangle}} \tag{3.30}$$

$$\int d\vec{r} \langle \Delta x(r) \Delta x(0) \rangle = \mathcal{O}(\xi^3) \tag{3.43}$$

The purpose of this course is to examine the cases where $V/\xi^3 = \mathcal{O}(1)$ and these results break down! It is worthwhile to give some toy examples now where, in particular, Eq. 3.43 breaks down.

where $n = 1$ is the solid-on-solid model, and $n = 2$ is the discrete Gaussian model. With Eq. 10.9, the partition function is

$$Z = \left(\prod_i \sum_{h_i} \right) e^{-\frac{J}{k_B T} \sum_{i'=1}^L |h_{i'} - h_{i'+1}|^2} \quad (10.11)$$

This is for $d = 2$, but the generalization to $d=3$ is easy. Note that

$$Z = Z\left(\frac{k_B T}{J}, L\right) \quad (10.12)$$

One can straight forwardly solve Z numerically. Analytically it is a little tough. It turns out to be easier to solve for the continuum version of Eq. 10.11 which we shall consider next.

10.2 Continuum Model of Surface

Instead of using a discrete mesh, let's do everything in the continuum limit. Let $h(\vec{x})$ be the height of the interface at any point \vec{x} as shown below. This

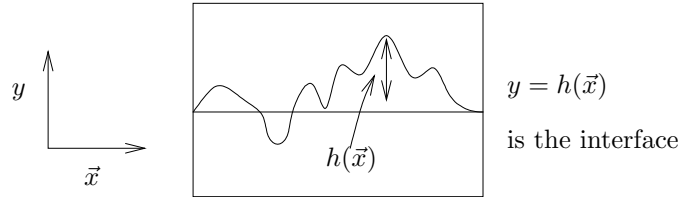


Figure 10.7:

is a useful description if there are no overhangs or bubbles, which cannot be described by $y = h(\vec{x})$. Of course, although it was not mentioned above, the

These give a multivalued $h(\vec{x})$, as shown

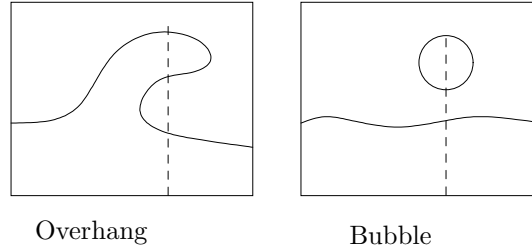


Figure 10.8:

“lattice model” (fig. 10.5) also could not have overhangs or bubbles. The states

the system can have any value of $h(\vec{x})$ at any point \vec{x} . The continuum analogue of Eq. 10.7 is

$$\begin{aligned} \sum_{\{states\}} &= \sum_{\{h_{\vec{x}}\}} = \prod_{\vec{x}} \int dh(\vec{x}) \\ &\equiv \int \int \mathcal{D}h(\cdot) \end{aligned} \quad (10.13)$$

where the last step just shows some common notation for $\prod_{\vec{x}} \int dh(\vec{x})$. Things are a little subtle because \vec{x} is a continuous variable, but we can work it through. One other weaselly point is that the sum over states is dimensionless, while $\prod_{\vec{x}} \int dh(\vec{x})$ has dimensions of $(\prod_x L)$. This constant factor of dimensionality does not affect our results, so we shall ignore it.

For the energy of a state, we shall simply make it proportional to the amount of area in a state $h(\vec{x})$, as shown in fig. 10.7.

$$E_{state}\{h(\vec{x})\} \propto (\text{Area of surface } y = h(\vec{x}))$$

or

$$E_{state} = \sigma(L')^{d-1} \quad (10.14)$$

where $(L')^{d-1}$ is the area of the surface $y = h(\vec{x})$, and σ is a positive constant.

It is worth stopping for a second to realize that this is consistent with our definition of excess free energy $\Delta F = \sigma L^{d-1}$. In fact, it almost seems a little too consistent, being essentially equal to the excess free energy!

This blurring of the distinction between microscopic energies and macroscopic free energies is common in modern work. It means we are considering a “coarse-grained” or *mesoscopic* description. Consider a simple example

$$e^{-F/k_B T} \equiv Z = \sum_{\{h\}} e^{-E_h/k_B T}$$

where h labels a state. Now say one has a large number of states which have the same energy E_h . Call these states, with the same E_h , H . Hence we can rewrite

$$\sum_{\{h\}} e^{-E_h/k_B T} = \sum_{\{H\}} g_H e^{-E_H/k_B T}$$

where

$$g_H = \# \text{ of states } h \text{ for state } H$$

Now let the local entropy

$$S = k_B \ln g_H$$

So we have

$$e^{-F/k_B T} = \sum_{\{H\}} e^{-F_H/k_B T}$$

where $F_H = E_H - TS_H$. This example is partially simple since we only partially summed states with the same energy. Nevertheless, the same logic applies if one

does a partial sum over states which might have different energies. this long digression is essentially to rationalize the common notation (instead of Eq. 10.14) of

$$E_{state} = F_{state} = \sigma(L')^{d-1} \quad (10.15)$$

Let us now calculate $(L')^{d-1}$ for a given surface $y = h(\vec{x})$

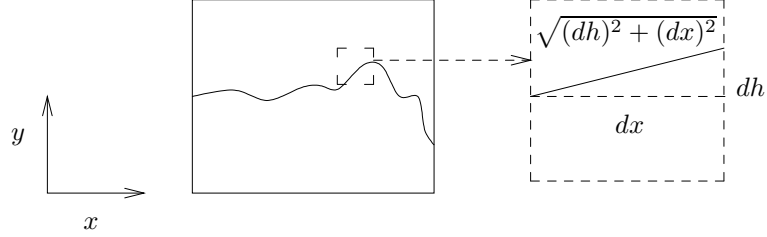


Figure 10.9:

As shown above, each element (in $d = 2$) of the surface is

$$\begin{aligned} dL' &= \sqrt{(dh)^2 + (dx)^2} \\ &= dx \sqrt{1 + \left(\frac{dh}{dx}\right)^2} \end{aligned} \quad (10.16)$$

In d -dimensions one has

$$d^{d-1}L' = d^{d-1}x \sqrt{1 + \left(\frac{\partial h}{\partial \vec{x}}\right)^2} \quad (10.17)$$

Integrating over the entire surface gives

$$(L')^{d-1} = \int d^{d-1}x \sqrt{1 + \left(\frac{\partial h}{\partial \vec{x}}\right)^2}$$

so that

$$E_{state} = \sigma \int d^{d-1}\vec{x} \sqrt{1 + \left(\frac{\partial h}{\partial \vec{x}}\right)^2} \quad (10.18)$$

Of course, we expect

$$\left(\frac{\partial h}{\partial \vec{x}}\right)^2 \ll 1 \quad (10.19)$$

(that is, that the surface is fairly flat), so expanding to lowest order gives

$$E_{state} = \sigma L^{d-1} + \underbrace{\frac{\sigma}{2} \int d^{d-1}\vec{x} \left(\frac{\partial h}{\partial \vec{x}}\right)^2}_{\text{Extra surface area due to fluctuation}} \quad (10.20)$$

The partition function is therefore,

$$Z = \sum_{\{\text{states}\}} e^{-E_{state}/k_B T}$$

or,

$$Z = e^{-\frac{\sigma L^{d-1}}{k_B T}} \left(\prod_{\vec{x}} \int dh(x) \right) \exp \frac{-\sigma}{2k_B T} \int d^{d-1}\vec{x} \left(\frac{\partial h}{\partial \vec{x}'} \right)^2 \quad (10.21)$$

This looks quite formidable now, but it is straightforward to evaluate. In particle physics it is called a free-field theory. Note the similarity to the discrete partition function of Eq. 10.11. The reason Eq. 10.21 is easy to evaluate is that it simply involves a large number of Gaussian integrals

$$\int dh e^{-ah^2}$$

As we know, Gaussian integrals only have two important moments,

$$\langle h(x) \rangle$$

and

$$\langle h(\vec{x}) h(\vec{x}') \rangle$$

All properties can be determined from knowledge of these two moments! However, space is translationally invariant and isotropic in the \vec{x} plane (the plane of the interface), so properties involving two points do not depend upon their

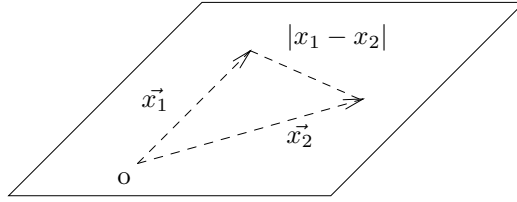


Figure 10.10: \vec{x} plane

exact positions, only the distance between them. That is

$$\langle h(x) \rangle = \text{const.}$$

and

$$\langle h(\vec{x}_1) h(\vec{x}_2) \rangle = G(|\vec{x}_1 - \vec{x}_2|) \quad (10.22)$$

For convenience, we can choose

$$\langle h \rangle = 0 \quad (10.23)$$

then our only task is to evaluate the correlation function

$$\begin{aligned} G(x) &= \langle h(\vec{x}) h(0) \rangle \\ &= \langle h(\vec{x} + \vec{x}') h(\vec{x}') \rangle \end{aligned} \quad (10.24)$$

To get $G(x)$, we use the partition function from Eq. 10.21, from which the probability of a state is

$$\rho_{state} \propto e^{\frac{-\sigma}{2k_B T} \int d^{d-1} \vec{x} (\frac{\partial h}{\partial \vec{x}})^2} \quad (10.25)$$

The subtle thing here is the gradients which mix the probability of $h(\vec{x})$ with that of a very near by $h(\vec{x}')$. Eventually this means we will use fourier transforms. To see this mixing, consider

$$\begin{aligned} \int d\vec{x} (\frac{\partial h}{\partial \vec{x}})^2 &= \int d\vec{x} [\frac{\partial}{\partial \vec{x}} \int d\vec{x}' h(\vec{x}') \delta(\vec{x} - \vec{x}')]^2 \\ &= \int d\vec{x} \int d\vec{x}' \int d\vec{x}'' h(\vec{x}) h(\vec{x}'') (\frac{\partial}{\partial \vec{x}} \delta(\vec{x} - \vec{x}')) \cdot (\frac{\partial}{\partial \vec{x}'} \delta(\vec{x} - \vec{x}')) \end{aligned}$$

Using simple properties of the Dirac delta function. Now let

$$\begin{aligned} x &\rightarrow x'' \\ x' &\rightarrow x \\ x'' &\rightarrow x' \end{aligned}$$

Since they are just dummy indices, giving

$$\begin{aligned} &= \int d\vec{x} \int d\vec{x}' \int d\vec{x}'' h(\vec{x}) h(\vec{x}') (\frac{\partial}{\partial \vec{x}''} \delta(\vec{x}'' - \vec{x})) \cdot (\frac{\partial}{\partial \vec{x}'} \delta(\vec{x}' - \vec{x})) \\ &= \int d\vec{x} \int d\vec{x}' \int d\vec{x}'' h(\vec{x}) h(\vec{x}') \frac{\partial}{\partial \vec{x}} \cdot \frac{\partial}{\partial \vec{x}'} (\delta(\vec{x}'' - \vec{x}) \delta(\vec{x}' - \vec{x})) \\ &= \int d\vec{x} \int d\vec{x}' h(\vec{x}) h(\vec{x}') \frac{\partial}{\partial \vec{x}} \cdot \frac{\partial}{\partial \vec{x}'} \delta(\vec{x} - \vec{x}') \\ &= \int d\vec{x} \int d\vec{x}' h(\vec{x}) h(\vec{x}') [-\frac{\partial^2}{\partial \vec{x}^2} \delta(\vec{x} - \vec{x}')] \end{aligned}$$

(you can do this by parts integration, and there will be terms involving surfaces at ∞ , which all vanish.) Hence,

$$\int d^{d-1} \vec{x} (\frac{\partial h}{\partial \vec{x}})^2 = \int d^{d-1} \vec{x} \int d^{d-1} \vec{x}' h(\vec{x}) M(\vec{x} - \vec{x}') h(\vec{x}') \quad (10.26)$$

where the interaction matrix,

$$M(\vec{x}) = -\frac{\partial^2}{\partial \vec{x}^2} \delta(\vec{x}) \quad (10.27)$$

which has the form shown in fig. 10.11. This “Mexican hat” interaction matrix appears in many different contexts. It causes $h(\vec{x})$ to interact with $h(\vec{x}')$.

In fourier space, gradients $\partial/\partial \vec{x}$ become numbers, or rather wave numbers \vec{k} . We will use this to simplify our project. It is convenient to introduce continuous

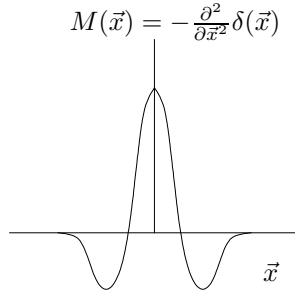


Figure 10.11:

and discrete fourier transforms. One or another is more convenient at a given time. We have,

$$h(\vec{x}) = \begin{cases} \int \frac{d^{d-1}\vec{k}}{(2\pi)^{d-1}} e^{i\vec{k}\cdot\vec{x}} \hat{h}(\vec{k}) & (Continuous) \\ \frac{1}{L^{d-1}} \sum_{\vec{k}} e^{i\vec{k}\cdot\vec{x}} \hat{h}_{\vec{k}} & (Discrete) \end{cases} \quad (10.28)$$

where

$$\begin{aligned} \hat{h}(\vec{k}) &= \int d^{d-1}\vec{x} e^{-i\vec{k}\cdot\vec{x}} h(\vec{x}) \\ &= \hat{h}_{\vec{k}} \end{aligned} \quad (10.29)$$

Closure requires

$$\delta(\vec{x}) = \begin{cases} \int \frac{d^{d-1}\vec{k}}{(2\pi)^{d-1}} e^{i\vec{k}\cdot\vec{x}} \\ \frac{1}{L^{d-1}} \sum_{\vec{k}} e^{i\vec{k}\cdot\vec{x}} \end{cases} \quad (10.30)$$

and

$$\delta(\vec{k}) = \int \frac{d^{d-1}\vec{x}}{(2\pi)^{d-1}} e^{i\vec{k}\cdot\vec{x}}$$

but

$$\delta_{\vec{k},0} = \frac{1}{L^{d-1}} \int d^{d-1}\vec{x} e^{i\vec{k}\cdot\vec{x}} \quad (10.31)$$

is the Kronecker delta

$$\delta_{\vec{k},0} = \begin{cases} 1 & , \text{ if } \vec{k} = 0 \\ 0 & , \text{ otherwise} \end{cases} \quad (10.32)$$

not the Dirac delta function.

We have used the density of states in \vec{k} space as

$$\left(\frac{L}{2\pi}\right)^{d-1}$$

so that the discrete \rightarrow continuum limit is

$$\sum_{\vec{k}} \rightarrow \left(\frac{L}{2\pi}\right)^{d-1} \int d^{d-1}\vec{k}$$

and

$$\delta_{\vec{k},0} \rightarrow \left(\frac{L}{2\pi}\right)^{d-1} \delta(\vec{k}) \quad (10.33)$$

Using the Fourier transforms we can simplify the form of E_{state} in Eq. 10.20. Consider

$$\begin{aligned} \int d^{d-1}\vec{x} \left(\frac{\partial h}{\partial \vec{x}}\right)^2 &= \\ &= \int d\vec{x} \left(\frac{\partial}{\partial \vec{x}} \int \frac{d\vec{k}}{(2\pi)^{d-1}} e^{i\vec{k}\cdot\vec{x}} \hat{h}(\vec{k})\right)^2 \\ &= \int d\vec{x} \int \frac{d\vec{k}}{(2\pi)^{d-1}} \int \frac{d\vec{k}'}{(2\pi)^{d-1}} (-\vec{k} \cdot \vec{k}') \hat{h}(\vec{k}) \hat{h}(\vec{k}') e^{i(\vec{k}+\vec{k}')\cdot\vec{x}} \\ &= \int \frac{d\vec{k}}{(2\pi)^{d-1}} \int \frac{d\vec{k}'}{(2\pi)^{d-1}} (-\vec{k} \cdot \vec{k}') \hat{h}(\vec{k}) \hat{h}(\vec{k}') \left[\int d\vec{x} e^{i(\vec{k}+\vec{k}')\cdot\vec{x}} \right] \\ &= \int \frac{d\vec{k}}{(2\pi)^{d-1}} k^2 \hat{h}(\vec{k}) \hat{h}(-\vec{k}) \end{aligned}$$

after doing \vec{k}' integral. But $h(\vec{x})$ is real, so $\hat{h}^*(\vec{k}) = \hat{h}(-\vec{k})$ (from Eq. 10.29), and we have

$$\int d^{d-1}\vec{x} \left(\frac{\partial h}{\partial \vec{x}}\right)^2 = \int \frac{d^{d-1}\vec{k}}{(2\pi)^{d-1}} k^2 |\hat{h}(\vec{k})|^2 \quad (\text{Continuum})$$

or

$$\int d^{d-1}\vec{x} \left(\frac{\partial h}{\partial \vec{x}}\right)^2 = \frac{1}{L^{d-1}} \sum_{\vec{k}} k^2 |\hat{h}_{\vec{k}}|^2 \quad (\text{Discrete}) \quad (10.34)$$

Hence modes of $\hat{h}_{\vec{k}}$ are *uncoupled* in fourier space; the matrix $M(\vec{x})$ has been replaced by the number k^2 , (see Eqs. 10.26 and 10.27). Therefore we have

$$E_{state} = \sigma L^{d-1} + \frac{\sigma}{2L^{d-1}} \sum_{\vec{k}} k^2 |\hat{h}_{\vec{k}}|^2 \quad (10.35)$$

For the partition function we need to sum out all the states $\sum_{\{states\}}$ using the fourier modes $\hat{h}_{\vec{k}}$ rather than $h(\vec{x})$. This is a little subtle because $h(\vec{x})$ is real while $\hat{h}_{\vec{k}}$ is complex. Of course not all the components are independent since $\hat{h}_{\vec{k}} = \hat{h}_{-\vec{k}}^*$, so we double count each mode. To do the sum properly we have

$$\sum_{\{states\}} = \prod_{\vec{x}} \int dh(\vec{x}) = \prod_{\vec{k}}' \int d^2 \hat{h}_{\vec{k}} \quad (10.36)$$

where $d^2 \hat{h}_k = d \Re \hat{h}_k d \Im \hat{h}_k$

and $\prod'_{\vec{k}} \leftarrow$ Restriction to half of \vec{k} space to avoid double counting

For the most part, this prime plays no role in the algebra below. Recall that

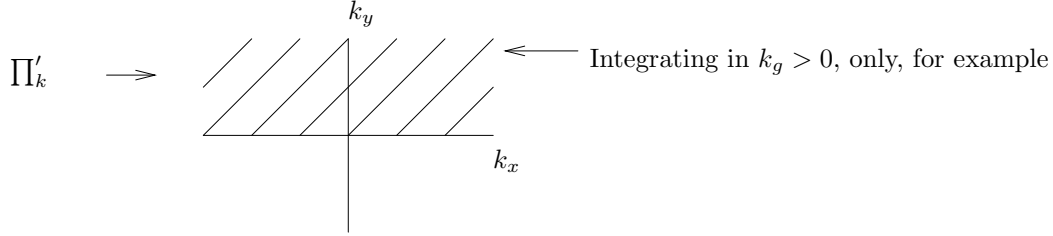


Figure 10.12:

the only nontrivial moment is

$$\begin{aligned} G(x) &= \langle h(\vec{x}) h(0) \rangle \\ &= \langle h(\vec{x} + \vec{x}') h(\vec{x}') \rangle \end{aligned}$$

from Eq. 10.23 above. This has a simple consequence for the Fourier mode correlation function

$$\langle \hat{h}(\vec{k}) \hat{h}(\vec{k}') \rangle$$

Note

$$\begin{aligned} \langle \hat{h}(\vec{k}) \hat{h}(\vec{k}') \rangle &= \int d^{d-1} \vec{x} \int d^{d-1} \vec{x}' e^{-i\vec{k} \cdot \vec{x} - i\vec{k}' \cdot \vec{x}'} \langle h(\vec{x}) h(\vec{x}') \rangle \\ &= \int d\vec{x} \int d\vec{x}' e^{-i\vec{k} \cdot \vec{x} - i\vec{k}' \cdot \vec{x}'} G(\vec{x} - \vec{x}') \end{aligned}$$

Let,

$$\begin{aligned} \vec{y} &= \vec{x} - \vec{x}' & \vec{x} &= \vec{y}' + \frac{1}{2}\vec{y} \\ \vec{y} &= \frac{1}{2}(\vec{x} + \vec{x}') & \vec{x}' &= \vec{y}' + \frac{1}{2}\vec{y} \end{aligned}$$

so that $d\vec{x}d\vec{x}' = d\vec{y}d\vec{y}'$, and

$$\langle \hat{h}(\vec{k}) \hat{h}(\vec{k}') \rangle = \int d\vec{y} e^{-i(\vec{k} - \vec{k}') \cdot \frac{\vec{y}}{2}} G(y) \times \int d\vec{y}' e^{-i(\vec{k} + \vec{k}') \cdot \vec{y}'}$$

so,

$$\begin{aligned} \langle \hat{h}(\vec{k}) \hat{h}(\vec{k}') \rangle &= \int d\vec{y} e^{-i\vec{k} \cdot \vec{y}} G(y) (2\pi)^{d-1} \delta(\vec{k} + \vec{k}') \\ &= \left[\int d\vec{x} e^{-i\vec{k} \cdot \vec{x}} G(\vec{x}) \right] (2\pi)^{d-1} \delta(\vec{k} + \vec{k}') \quad , \text{ letting } \vec{y} \rightarrow \vec{x} \end{aligned}$$

as

$$\langle \hat{h}(\vec{k}) \hat{h}(\vec{k}') \rangle = \begin{cases} \hat{G}(\vec{k}) (2\pi)^{d-1} \delta(\vec{k} + \vec{k}') & (Continuum) \\ \hat{G}_{\vec{k}} L^{d-1} \delta_{\vec{k}+\vec{k}', 0} & (Discrete) \end{cases} \quad (10.37)$$

Hence, in Fourier space, the only non-zero Fourier cos is

$$\langle \hat{h}_{\vec{k}} \hat{h}_{-\vec{k}} \rangle = \langle |\hat{h}_{\vec{k}}|^2 \rangle$$

which is directly related to $\hat{G}_{\vec{k}}$. Using the probability

$$\rho_{state} \propto e^{-\frac{\sigma}{2k_B T L^{d-1}} \sum_{\vec{k}} k^2 |\hat{h}_{\vec{k}}|^2}$$

we have,

$$\langle |\hat{h}_{\vec{k}}|^2 \rangle = \frac{\prod_{\vec{k}'} \int d^2 \hat{h}_{\vec{k}'} |\hat{h}_{\vec{k}}|^2 e^{-\frac{\sigma}{2k_B T L^{d-1}} \sum_{\vec{k}'} k'^2 |\hat{h}_{\vec{k}'}|^2}}{\prod_{\vec{k}'} \int d^2 \hat{h}_{\vec{k}'} e^{-\frac{\sigma}{2k_B T L^{d-1}} \sum_{\vec{k}'} k'^2 |\hat{h}_{\vec{k}'}|^2}} \quad (10.38)$$

Except for the integrals involving $\hat{h}_{\vec{k}}$, everything on the numerator and denominator cancels out. We have to be careful with real and imaginary parts though. Consider

$$\sum_k k^2 |\hat{h}_k|^2 = \sum_k k^2 \hat{h}_k \hat{h}_{-k}$$

For the particular term involving \hat{h}_{15} , for example

$$(15)^2 \hat{h}_{15} \hat{h}_{-15} + (-15)^2 \hat{h}_{-15} \hat{h}_{-15} = 2(15)^2 \hat{h}_{15} \hat{h}_{-15}$$

giving a factor of 2. In any case,

$$\langle |\hat{h}_{\vec{k}}|^2 \rangle = \frac{\int d^2 \hat{h}_{\vec{k}} |\hat{h}_{\vec{k}}|^2 e^{-\frac{2\sigma}{2k_B T L^{d-1}} k^2 |\hat{h}_{\vec{k}}|^2}}{\int d^2 \hat{h}_{\vec{k}} e^{-\frac{2\sigma}{2k_B T L^{d-1}} k^2 |\hat{h}_{\vec{k}}|^2}}$$

(These steps are given in Goldenfeld's book in Section 6.3, p.174.) Now let

$$\hat{h}_{\vec{k}} = R e^{i\theta}$$

so that

$$\langle |\hat{h}_k|^2 \rangle = \frac{\int_0^\infty R dR R^2 e^{-R^2/a}}{\int_0^\infty R dR e^{-R^2/a}}$$

where

$$a = \frac{k_B T}{\sigma k^2} \frac{1}{L^{d-1}} \quad (10.39)$$

A little fiddling gives

$$\langle |\hat{h}_k|^2 \rangle = a = \frac{k_B T}{\sigma k^2} \frac{1}{L^{d-1}}$$

Hence we obtain, from Eq. 10.37

$$\langle \hat{h}(\vec{k}) \hat{h}(\vec{k}') \rangle = \hat{G}(\vec{k}) (2\pi)^{d-1} \delta(\vec{k} + \vec{k}')$$

where

$$\hat{G}(\vec{k}) = \frac{k_B T}{\sigma} \frac{1}{k^2}$$

and

$$G(x) = \langle h(\vec{x}) h(0) \rangle \quad (10.40)$$

From this correlation function we will obtain the width of the surface. We will

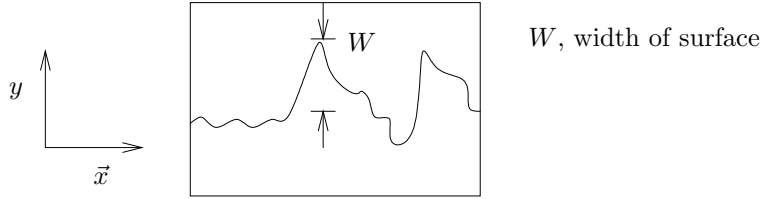


Figure 10.13:

define the width to be the root-mean-square of the height fluctuations averaged over the \vec{x} plane. That is

$$w^2 = \frac{1}{L^{d-1}} \int d^{d-1} \vec{x} \langle (h(\vec{x}) - \langle h(\vec{x}) \rangle)^2 \rangle \quad (10.41)$$

which is overcomplicated for our case, since $\langle h(\vec{x}) \rangle = 0$, and $\langle h(\vec{x}) h(\vec{x}) \rangle = G(0)$, from above. So we have the simpler form

$$w^2 = G(0) \quad (10.42)$$

From the definition of fourier transform,

$$G(0) = \int \frac{d^{d-1} \vec{k}}{(2\pi)^{d-1}} \frac{k_B T}{\sigma k^2} \quad (10.43)$$

which has a potential divergence as $\vec{k} \rightarrow 0$, or $\vec{k} \rightarrow \infty$. We shall always restrict our integrations so that

$$\underbrace{\frac{2\pi}{L}}_{\text{System size}} \leq |\vec{k}| \leq \underbrace{\Lambda}_{\text{Lattice constant}} \quad (10.44)$$

Then it is easy to do the integral of Eq. 10.43. First in $d = 2$,

$$\begin{aligned} G(0) &= \frac{k_B T}{\sigma} \frac{1}{2\pi} \int_{-\Lambda}^{\Lambda} dk \frac{1}{k^2} \\ &= \frac{k_B T}{\pi \sigma} \int_{\frac{2\pi}{L}}^{\Lambda} dk \frac{1}{k^2} \end{aligned}$$

and

$$G(0) = \frac{k_B T}{2\pi^2 \sigma} L, \quad d = 2$$

so

$$w = \sqrt{\frac{k_B T}{2\pi^2 \sigma}} L^{1/2}, \quad d = 2 \quad (10.45)$$

Similarly, in $d = 3$,

$$G(0) = \frac{k_B T}{\sigma} \frac{1}{4\pi^2} 2\pi \int_{\frac{2\pi}{L}}^{\Lambda} \frac{k dk}{k^2}$$

and

$$G(0) = \frac{k_B T}{2\pi \sigma} \ln(L\Lambda/2\pi), \quad d = 3$$

so,

$$w = \sqrt{\frac{k_B T}{2\pi \sigma}} \left(\ln \frac{L\Lambda}{2\pi}\right)^{1/2}, \quad d = 3 \quad (10.46)$$

It is easy to obtain L dependences as dimension of space varies. One obtains,

$$w = \begin{cases} \text{undefined}, & d \leq 1 \\ L^X, & 1 < d < 3 \\ (\ln L)^{1/2}, & d = 3 \\ \text{const.}, & d > 3 \end{cases} \quad (10.47)$$

where

$$X = \frac{3-d}{2} \quad (10.48)$$

is called the roughening exponent. The fact that w is undefined for $d \leq 1$ is explained below.

Eq. 10.47 implies the interface is rough and increases with L for $d \leq 3$. However, note that the width (for $d > 1$) is not large compared to the system

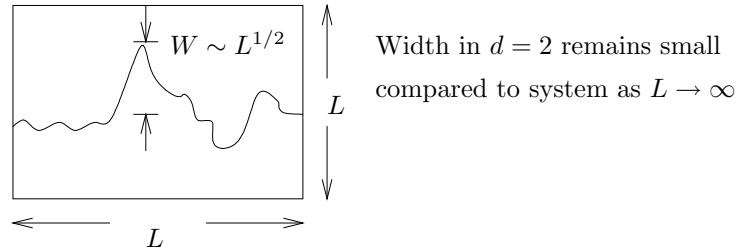


Figure 10.14:

itself, as $L \rightarrow \infty$.

$$\frac{w}{L} = \frac{1}{L^{1-X}} = \frac{1}{L^{(d-1)/2}} \quad (10.49)$$

Hence the width is small for $d > 1$. In $d = 1$, it appears the width is comparable to the system size! This means the interface — and indeed phase coexistence

itself — does not exist in $d = 1$. This is one signature of a *lower critical dimension*, at and below which, phase coexistence cannot occur at any nonzero temperature.

In general, one defines the roughening exponent X by

$$w \sim L^X \quad (10.50)$$

as $L \rightarrow \infty$. This is equivalent to the definition of the surface correlation exponent η_s

$$G(\vec{k}) \sim \frac{1}{k^{2-\eta_s}} \quad (10.51)$$

as $k \rightarrow 0$. (Here $\eta_s = 0$, of course.) The two exponents are related by the formula

$$X = \frac{3-d}{2} - \frac{\eta_s}{2} \quad (10.52)$$

The surface turns out to be self-affine, in the way we discussed earlier for the Von Koch snowflake, since correlation functions like $\hat{G}(\vec{k})$ are power-law like. The self-affine dimension of the rough surface is

$$d_s = X + d - 1 \quad (10.53)$$

To obtain the correlation function in real space is a little awkward because of the divergence of $G(X \rightarrow 0)$ as $L \rightarrow 0$. For convenience, consider

$$g(x) \equiv \langle (h(\vec{x}) - h(0))^2 \rangle \quad (10.54)$$

Multiplying this out gives

$$g(x) = 2(\langle h^2 \rangle - \langle h(\vec{x})h(0) \rangle)$$

This is simply

$$g(x) = \begin{cases} 2(G(0) - G(x)) \\ \text{or} \\ 2(w^2 - G(x)) \end{cases} \quad (10.55)$$

The interpretation of $g(x)$ from Eq. 10.54 is simple, it is the (squared) difference in the heights between two points a distance x apart, as shown in fig. 10.15. Not surprisingly, we expect (for large L)

$$g(x \rightarrow L) = 2w^2 \quad (10.56)$$

since, $G(L) = \langle h(L) h(0) \rangle = \langle h(L) \rangle \langle h(0) \rangle$ because the points 0 and L are so far apart so as to be uncorrelated, so $G(L) = 0$.

In any case, we have

$$\begin{aligned} g(x) &= 2 \frac{k_B T}{\sigma} \frac{1}{(2\pi)^{d-1}} \int d^{d-1} \vec{k} \left(\frac{1 - e^{i\vec{k} \cdot \vec{x}}}{k^2} \right) \\ &= 2 \frac{k_B T}{\sigma} \frac{1}{(2\pi)^{d-1}} \int d^{d-1} \vec{k} \left(\frac{1 - \cos \vec{k} \cdot \vec{x}}{k^2} \right) \end{aligned} \quad (10.57)$$

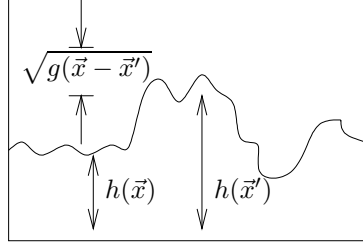


Figure 10.15:

Consider $d = 2$. Let

$$\begin{aligned} g(x) &= 2 \frac{k_B T}{\sigma} \frac{1}{2\pi} \int_{-\Lambda}^{\Lambda} dk \left(\frac{1 - \cos kx}{k^2} \right) \\ &= 2 \frac{k_B T}{\pi \sigma} \int_{2\pi/L}^{\Lambda} dk \frac{1 - \cos kx}{k^2} \end{aligned}$$

let $u = kx$

$$g(x) = 2 \frac{k_B T}{\pi \sigma} x \left\{ \int_{2\pi x/L}^{\Lambda x} du \frac{1 - \cos u}{u^2} \right\}$$

let $\Lambda \rightarrow \infty$ and $L \rightarrow \infty$ in the integral (for convenience)

$$g(x) = 2 \frac{k_B T}{\pi \sigma} x \underbrace{\left(\int_0^{\infty} du \frac{1 - \cos u}{u^2} \right)}_{\pi/2}$$

so,

$$g(x) = \frac{k_B T}{\sigma} x, \quad d = 2 \quad (10.58)$$

In $d = 3$,

$$g(x) = 2 \frac{k_B T}{\sigma} \frac{1}{4\pi^2} \int_0^{2\pi} d\theta \int_{2\pi/L}^{\Lambda} k dk \left(\frac{1 - \cos kx \cos \theta}{k^2} \right)$$

This is a little more involved, and I will just quote the answer

$$g(x) = \frac{k_B T}{4\pi \sigma} \ln x \Lambda, \quad d = 3 \quad (10.59)$$

In general, one obtains

$$g(x) = \begin{cases} \text{undefined}, & d = 1 \\ x^{2X}, & 1 < d < 3 \\ \ln x, & d = 3 \\ \text{const.}, & d > 3 \end{cases} \quad (10.60)$$

where, again $X = (3 - d)/2$. This confirms our earlier claim that correlations are power — law like.

(There is a subtlety here involving constraints which deserves a minute of time. The limit $g(x \rightarrow L) \sim L^{2X}$, but the constraint is not the same as $2w^2$ as derived above. Reconsider the integral of Eq. 10.58:

$$g(x) = 2 \frac{k_B T}{\pi \sigma} x \left\{ \int_{\frac{2\pi x}{L}}^{\Lambda x} du \frac{1 - \cos u}{u^2} \right\}$$

Now *just* let $\Lambda = \infty$. Rewriting gives

$$\begin{aligned} g(x) &= 2 \frac{k_B T}{\pi \sigma} x \left\{ \int_0^\infty du \frac{1 - \cos u}{u^2} - \int_0^{\frac{2\pi x}{L}} du \frac{1 - \cos u}{u^2} \right\} \\ &= 2 \frac{k_B T}{\pi \sigma} x \left\{ \frac{\pi}{2} - \int_0^{\frac{2\pi x}{L}} du \frac{1 - \cos u}{u^2} \right\} \end{aligned}$$

or, for $d = 2$

$$g(x, L) = \frac{k_B T}{\sigma} x f(x/L) \quad (10.61)$$

where

$$f(x) = 1 - \frac{2}{\pi} \int_0^{2\pi x} du \frac{1 - \cos u}{u^2} \quad (10.62)$$

Note that

$$f(x \rightarrow \infty) = 0$$

but

$$f(x \rightarrow 0) = 1$$

This is called a scaling function. End of digression.)

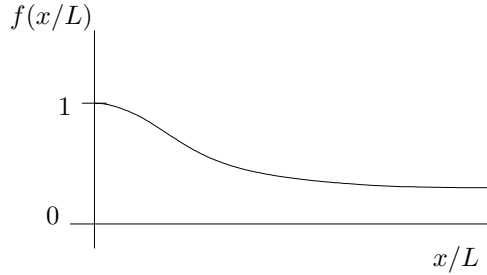


Figure 10.16:

We are pretty well done now, except we shall calculate the “renormalized” surface tension from the partition function. Recall from Eq. 10.21

$$Z = e^{-\frac{\sigma L^{d-1}}{k_B T}} \left(\prod_{\vec{x}} \int dh(x) \exp \frac{-\sigma}{2k_B T} \int d^{d-1} \vec{x} \left(\frac{\partial h}{\partial \vec{x}'} \right)^2 \right)$$

Switching to Fourier space using Eqs. 10.34 and 10.36 gives

$$\begin{aligned} Z &= e^{-\frac{\sigma L^{d-1}}{k_B T}} \left(\prod_{\vec{k}} \int d^2 \hat{h}_{\vec{k}} \right) \exp \frac{-\sigma}{2k_B T} \frac{1}{L^{d-1}} \sum_k k^2 |\hat{h}_k|^2 \\ &\equiv e^{-F/k_B T} \end{aligned} \quad (10.63)$$

So calculating Z gives the thermodynamic free energy F . We will call the “renormalized”, or more properly the thermodynamic surface tension σ^*

$$\sigma^* \equiv \left(\frac{\partial F}{\partial A} \right)_{T, V, N}$$

or,

$$\sigma^* = \left(\frac{\partial F}{\partial L^{d-1}} \right)_{T, V, N} \quad (10.64)$$

going back to Eq. 10.63

$$Z = e^{-\frac{\sigma L^{d-1}}{k_B T}} \prod_{\vec{k}} \int d^2 \hat{h}_{\vec{k}} e^{-\frac{\sigma}{2k_B T} \frac{k^2}{L^{d-1}} |\hat{h}_k|^2}$$

Since all modes are independent. But

$$\int d^2 \hat{h}_{\vec{k}} = \int_{-\infty}^{\infty} d\Re \hat{h}_{\vec{k}} \int_{-\infty}^{\infty} d\Im \hat{h}_{\vec{k}}$$

or if $\hat{h}_{\vec{k}} = R e^{i\theta}$

$$\int d^2 \hat{h}_k = \int_0^{2\pi} d\theta \int_0^{\infty} R dR \quad (10.65)$$

Hence

$$Z = e^{-\frac{\sigma L^{d-1}}{k_B T}} \prod_{\vec{k}} \int_0^{2\pi} d\theta \int_0^{\infty} R dR e^{-(\frac{\sigma}{2k_B T} \frac{k^2}{L^{d-1}}) R^2}$$

$$\text{let } u = \left(\frac{\sigma}{2k_B T} \frac{k^2}{L^{d-1}} \right) R^2$$

$$\begin{aligned} Z &= e^{-\frac{\sigma L^{d-1}}{k_B T}} \prod_{\vec{k}} \int_0^{2\pi} d\theta \frac{1}{2 \left(\frac{\sigma}{2k_B T} \frac{k^2}{L^{d-1}} \right)} \int_0^{\infty} du e^{-u} \\ &= e^{-\frac{\sigma L^{d-1}}{k_B T}} \prod_{\vec{k}} \int_0^{2\pi} d\theta \frac{2\pi k_B T L^{d-1}}{\sigma k^2} \\ &= e^{-\frac{\sigma L^{d-1}}{k_B T}} e^{\ln \prod_{\vec{k}} \frac{2\pi k_B T L^{d-1}}{\sigma k^2}} \\ &= \exp \left(-\frac{\sigma L^{d-1}}{k_B T} + \sum_{\vec{k}} \ln \frac{2\pi k_B T L^{d-1}}{\sigma k^2} \right) \end{aligned}$$

$$Z = \exp\left(-\frac{\sigma L^{d-1}}{k_B T} + \frac{1}{2} \sum_{\vec{k}} \ln \frac{2\pi k_B T L^{d-1}}{\sigma k^2}\right) \quad (10.66)$$

But, $Z = \exp(-F/k_B T)$, up to a constant, so

$$F = \sigma L^{d-1} - \frac{k_B T}{2} \sum_{\vec{k}} \ln \frac{2\pi k_B T L^{d-1}}{\sigma k^2} \quad (10.67)$$

is the free energy due to the surface. The second term gives the contribution due to fluctuations. To take the derivative with respect to $\partial/\partial L^{d-1}$, it is important to note that the \vec{k} 's get shifted with L 's, and that it is the (kL) combination which is *not* a function of L . So to take the derivative, we rewrite

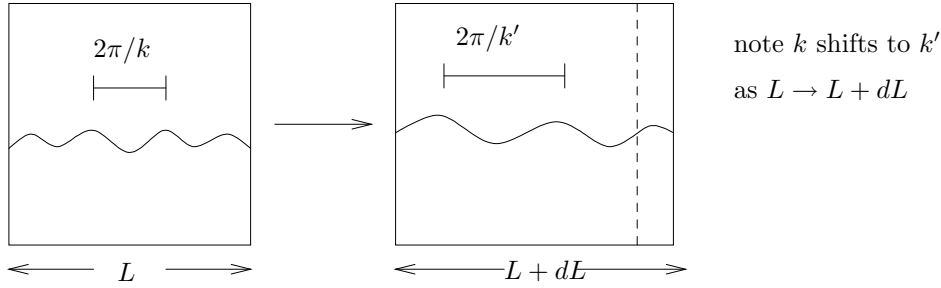


Figure 10.17:

$$F = \sigma L^{d-1} - \frac{k_B T}{2} \sum_{\vec{k}} \ln \frac{2\pi k_B T L^{d-1}}{\sigma (kL)^2}$$

or,

$$F = \sigma L^{d-1} - \frac{k_B T}{2} \sum_{\vec{k}} \ln(L^{d-1})^{(d+1)/(d-1)} - \frac{k_B T}{2} \sum_{\vec{k}} \ln \frac{2\pi k_B T}{\sigma (kL)^2}$$

or,

$$F = \sigma L^{d-1} - \frac{k_B T}{2} \left(\frac{d+1}{d-1}\right) (\ln L^{d-1}) \sum_{\vec{k}} - \frac{k_B T}{2} \sum_{\vec{k}} \ln \frac{2\pi k_B T}{\sigma (kL)^2} \quad (10.68)$$

The last term is independent of L^{d-1} , so taking the derivative $(\frac{\partial F}{\partial L^{d-1}})_{T,V,N} = \sigma^*$ gives,

$$\sigma^* = \sigma - \frac{k_B T}{2} \frac{d+1}{d-1} \left(\frac{1}{L^{d-1}} \sum_{\vec{k}} \right)_{(Discrete)}$$

or,

$$\sigma^* = \sigma - \frac{k_B T}{2} \frac{d+1}{d-1} \left(\int \frac{d^{d-1} \vec{k}}{(2\pi)^{d-1}} \right)_{(Continuum)} \quad (10.69)$$

is the renormalized surface tension. Note that fluctuations decrease the value of σ to the lower σ^* .

$$\text{In } d = 2, \int \frac{d^{d-1}\vec{k}}{(2\pi)^{d-1}} = \frac{1}{2\pi} \int_{-\Lambda}^{\Lambda} dk = \frac{\Lambda}{\pi} \quad (10.70)$$

$$\text{In } d = 3, \int \frac{d^{d-1}\vec{k}}{(2\pi)^{d-1}} = \frac{1}{4\pi^2} \int_0^{2\pi} d\theta \int_0^{\Lambda} k dk = \frac{1}{4\pi^2} \pi \Lambda^2 = \frac{\Lambda^2}{4\pi} \quad (10.71)$$

$$\text{In } d = 1, \int \frac{d^{d-1}\vec{k}}{(2\pi)^{d-1}} = 1 \quad (10.72)$$

Hence we have,

$$\sigma^* = \sigma - \frac{3k_B T}{2\pi} \Lambda \quad , d = 2$$

$$\sigma^* = \sigma - \frac{k_B T}{4\pi} \Lambda^2 \quad , d = 3$$

and since $d = 1$ is odd, let $d = 1 + \epsilon$, for very small ϵ , and

$$\sigma^* = \sigma - \frac{k_B T}{\epsilon} \quad , d = 1 + \epsilon, \epsilon \ll 1 \quad (10.73)$$

(It is worth noting that this is the first term in the $d = 1 + \epsilon$ expansion, where we have only considered the leading term in $E_{State} = \sigma \int d^{d-1}\vec{x} \sqrt{1 + (\frac{\partial h}{\partial \vec{x}})^2} \approx \sigma L^{d-1} + \frac{\sigma}{2} \int d^{d-1}\vec{x} (\frac{\partial h}{\partial \vec{x}})^2 + \dots$)

10.3 Impossibility of Phase Coexistence in $d=1$

Note that, again, the renormalized surface tension vanishes as $d \rightarrow 1$ (as $\epsilon \rightarrow 0$). In our simple calculation σ^* actually becomes negative infinity at $d = 1$.

In fact, the lack of phase coexistence in $d = 1$ is a theorem due to Landau and Pekar, which is worth quickly proving. (See Goldenfeld's book, p.46.)

A homogeneous phase has an energy

$$E_{Bulk} \propto +L^{d-1} \quad (10.74)$$

Putting in a surface gives an extra energy

$$E_{Surface} \propto +L^{d-1} \quad (10.75)$$

So the extra energy one gets due to adding a surface is

$$\begin{aligned} \Delta E_{1Surface} &\propto +L^{d-1} \\ \text{In } d = 1, \Delta E_{1Surface} &\propto +\mathcal{O}(1) \end{aligned} \quad (10.76)$$