Systems of interacting particles

So far, we mostly dealt with the systems where the particles (or states) did not have interactions with each other. This is clearly an idealisation (or the lowest density limit). Can we do better?

The total energy of the system is now

$$E = \sum_i \frac{p_i^2}{2m} + \sum_{i,j} \phi(x_i - x_j)$$

We can’t deal with too many of interacting particles, but let’s consider a grand canonical ensemble:

$$Z = \sum_{N=0}^{TOTAL} \left( e^{\frac{\beta E}{k_B}} Z(N) \right) = 1 + e^{\beta \mu} \sum_{\text{particle } [1]} e^{\frac{p_i^2}{2m k_B T}} + \frac{1}{2} e^{2\beta \mu} \sum_{\text{particle } [1] \text{ particle } [2]} e^{\frac{p_i^2}{2m k_B T}} e^{\frac{p_j^2}{2m k_B T}} e^{-\frac{\phi(x_i - x_j)}{k_B T}} + ...$$

Looking for the corresponding (grand) thermodynamic potential, in the classical regime we have the

$$e^{\beta \mu} \ll 1$$

$$\Phi = -k_B T \ln(1 + \Theta) = -k_B T \left( \Theta - \frac{1}{2} \Theta^2 \right)$$

$$= -k_B T \left( e^{\beta \mu} Z_1 + \frac{1}{2} e^{\beta \mu} \sum_{[1]} e^{\frac{p_i^2}{2m k_B T}} e^{-\frac{\phi(x_i-x_j)}{k_B T}} -1 \right)$$

Here we can actually integrate over both momenta, and the CoM position
Virial expansion

Particles interacting via the pair potential: \[ E = \sum_i \frac{p_i^2}{2m} + \sum_{i,j} \phi(x_i - x_j) \]

\[ \Phi = -k_B T \left( e^{\beta \mu} \sum_i e^{-\frac{p_i^2}{2m k_B T}} + \frac{1}{2} e^{2\beta \mu} \sum_{i,j} e^{\frac{p_i^2}{2m k_B T}} e^{\frac{p_j^2}{2m k_B T}} \left[ e^{\frac{\phi(x_i - x_j)}{k_B T}} - 1 \right] \right) \]

And also

\[ N = -\frac{\partial \Phi}{\partial \mu} = e^{\beta \mu} \sum_i e^{-\frac{p_i^2}{2m k_B T}} + e^{2\beta \mu} \sum_{i,j} e^{\frac{p_i^2}{2m k_B T}} e^{\frac{p_j^2}{2m k_B T}} \left[ e^{\frac{\phi(x_i - x_j)}{k_B T}} - 1 \right] \]

Here we can actually integrate over both momenta, and the CoM position

e.g. \[ \Phi = -k_B T \left( e^{\beta \mu V} \frac{e^{\beta \mu}}{\lambda^3} + \frac{1}{2} \left( \frac{e^{\beta \mu}}{\lambda^3} \right)^2 V \int d^3r e^{-\beta \mu(r)} - 1 \right) + ... \]

Define the virial coefficient: \[ B(T) = \frac{1}{2} \int d^3r [1 - e^{-\beta \mu(r)}] \]

Then \[ \Phi = -k_B T \cdot e^{\beta \mu} \frac{V}{\lambda^3} \left( 1 - \frac{e^{\beta \mu}}{\lambda^3} B(T) + ... \right) \]

Virial expansion

Particles interacting via the pair potential: \[ E = \sum_i \frac{p_i^2}{2m} + \sum_{i,j} \phi(x_i - x_j) \]

\[ \Phi = -k_B T \cdot e^{\beta \mu} V \left( 1 - \frac{e^{\beta \mu}}{\lambda^3} B(T) + ... \right) \quad \text{where} \quad B(T) = \frac{1}{2} \int d^3r [1 - e^{-\beta \mu(r)}] \]

Now let us examine how this affects thermodynamic properties of our interacting system:

\[ N = -\frac{\partial \Phi}{\partial \mu} = e^{\beta \mu} V \left( 1 - \frac{e^{\beta \mu}}{\lambda^3} B(T) + ... \right) \]

Also the pressure (equation of state)

\[ p = \frac{N}{V} \frac{k_B T}{V} \left( 1 + \frac{N}{V} B(T) + ... \right) = \frac{N k_B T}{V} \cdot \frac{\frac{1}{2} \int d^3r [1 - e^{-\beta \mu(r)}]}{1 - 2 \frac{N}{V} B(T)} \]

An alternative analysis from the canonical ensemble (handout) gives \( Z(\phi) \), and the expansion

\[ U = -\frac{\partial}{\partial \beta} \ln Z = \frac{3}{2} N k_B T + \frac{N^2}{V} k_B T \cdot B(T) + ... \]
Pair correlation function

In a dense system, with (identical) particles interacting via a pair potential \( \phi(x) \), e.g. long-range attraction + short-range repulsion, the canonical partition function is:

\[
Z = \sum_{\text{microstates}} e^{-\beta E(p,s)} = \frac{1}{N!} \left( \int \frac{d^3 p}{(2\pi)^3} e^{-\frac{p^2}{2m_0^2}} \right)^N \prod_i \int d^3 x_i \ e^{-\frac{1}{2kT} \sum_{ji} \phi(x_i-x_j)}
\]

\[
Z = \frac{1}{N!} \left( \frac{1}{\lambda^3} \right)^N \cdot Z_\phi
\]

The probability to find a particle at \( \{ x \} \) is, as usual,

\[
P(x_i) = \frac{N}{Z} \int d^3 x_i d^3 x_j d^3 x_k ... e^{-\frac{1}{kT} \sum_{ji} \phi(x_i-x_j)}
\]

The two-particle distribution function is the probability that there is a particle at \( \{ x_1 \} \) and another at \( \{ x_2 \} \) is

\[
P(x_1, x_2) = \frac{N(N-1)}{Z} \int d^3 x_1 d^3 x_2 d^3 x_3 ... e^{-\frac{1}{kT} \sum_{ji} \phi(x_i-x_j)}
\]

Define the (non-dimensional) radial distribution function

\[
g(r_1 - r_2) = \frac{V^2}{N^2} P(r_1, r_2)
\]

\[
P(1,2) = \frac{N(N-1)}{Z} \int d^3 x_1 d^3 x_2 d^3 x_3 ... e^{-\frac{1}{kT} \sum_{ji} \phi(x_i-x_j)}
\]

No interactions, \( \phi(x) = 0 \):

\[
g_0(r_1 - r_2) = \frac{V^2}{N^2} \frac{V^{N-2}}{V^N} \rightarrow 1
\]

Dense disordered liquid with \( \phi(x) \):

\[
g_0(r_1 - r_2) \propto e^{-\beta \phi(x_i-x_j)} \cdot \int e^{-\beta \phi(x_i-x_j)} d^3 x_i \int e^{-\beta \phi(x_i-x_j)} d^3 y
\]

Crystalline solid with \( \phi(x) \):

\[
g(r_1 - r_2) \propto \frac{1}{L^{N-1}} \int e^{-\beta \phi(x_i-x_j)} d^3 x_i \int e^{-\beta \phi(x_i-x_j)} d^3 y
\]

Lattice spacing

Thermal fluctuations

\( |r_1 - r_2| \)

\( |r_1 - r_2| \)
Van der Waals gas, again

Let’s divide the pair potential $\phi(x)$ into rigid short-range repulsion part $\phi_r(x)$ and a soft long-range attraction part $\phi_a(x)$:

$$Z = \frac{1}{N!} \left( \frac{1}{\lambda^3} \right)^N \int \prod_i d^3 x_i \ e^{-\frac{1}{\lambda^3} \sum_{ij} \phi (x_i - x_j)}$$

Instead of attempting to integrate, let’s say that each particle feels long-range attraction from many others, so:

$$\sum_{ij} \phi (x_i - x_j) = \frac{1}{2} \sum_{ij} \phi (x_i - x_j) = \frac{N(N-1)}{2} \int \phi (r) d^3 r \Rightarrow \frac{N^2}{V} a$$

The remaining $x_i$-integrals over volume(s) are reduced by exclusion of the repulsive volume around each particle:

$$\int \prod_i d^3 x_i \ e^{-\frac{1}{\lambda^3} \sum_{ij} \phi (x_i - x_j)} = (V-Nb)^N$$

We now have:

$$Z = \frac{1}{N!} \left( \frac{1}{\lambda^3} \right)^N (V-Nb)^N e^{\frac{N^2 a}{V}}$$

Second virial coefficient, again

This has been formally defined for:

$$\Phi = -k_b T \cdot \sum_{i} \phi(x_i - x_j) = \sum_{i} \phi(x_i - x_j)$$

Leading to the equation of state

$$p = \frac{N k_b T}{V} \left( 1 + \frac{N}{V} B(T) + ... \right)$$

How does this compare with the VdW equation of state?

$$p = \frac{N k_b T}{V-Nb} - \frac{N^2 a}{V^2} = \frac{N}{V} k_b T + \frac{N^2}{V^2} k_b T \left( b - \frac{a}{k_b T} \right) + ...$$

The second virial coefficient has to be a function of temperature, with $B(T)>0$ at high-$T$, and $B(T)<0$ at low-$T$ (as long as there is an attractive potential).
**Mixing of interacting species**

In earlier lectures, we have derived and briefly explored the concept of mixing entropy, which accounts for the increase of "number of conformations" $\Omega$ when different species are present and interchanging:

$$S_{\text{mix}} = k_B \ln \Omega = -Nk_B \sum_{\text{species } i} c_i \ln c_i$$

where $c_i = N_i/N$ and $N = \sum_i N_i$.

Taking an example of just two species mixing, it is easy to see how $S$ increases:

$$S_{\text{mix}} = -Nk_B \left( c_1 \ln c_1 + [1-c_1] \ln [1-c_1] \right)$$

(since $c_2 = 1-c_1$)

However, this is no longer an ideal gas: the molecules of each species now interact – with each other, and with the other species. The full energy is the sum of the three, with the $N=N_1+N_2$ a common factor:

$$U_{\text{int}} = U_{11} + U_{22} + U_{12} = N \left[ \frac{N_1^2}{V} k_BT \cdot B_{11}(T) + \frac{N_2^2}{V} k_BT \cdot B_{22}(T) + 2 \frac{N_1 N_2}{V^2} k_BT \cdot B_{12}(T) \right]$$

The difference is the potential energy of mixing:

$$U_{\text{mix}} = N \left[ 2 \epsilon_{12} - \epsilon_{11} - \epsilon_{22} \right] c_1 (1-c_1)$$
Free energy and pressure

The so-called “Flory-Huggins” theory of phase separation starts with composing the proper free energy function:

\[ F_{\text{mix}} = U_{\text{mix}} - T S_{\text{mix}} = N k_B T \left( \chi \cdot c_1 (1 - c_1) + c_1 \ln c_1 + [1 - c_1] \ln [1 - c_1] \right) \]

where \( \chi = \frac{1}{k_B T} \left[ 2 \varepsilon_{12} - \varepsilon_{11} - \varepsilon_{22} \right] \) is the non-dimensional shorthand, called the Flory \( \chi \)-parameter.

Osmotic pressure in the mixture:

\[ \Pi = -\frac{\partial F_{\text{mix}}}{\partial V} = -\frac{k_B T}{V_0} \frac{\partial F_{\text{mix}}}{\partial N} = \frac{k_B T}{V_0} \left[ \ln (1 - c_1) + \chi c_1^2 \right] \]

since \( c_1 = N_1 / N \)

At small concentration of the species \{1\} osmotic pressure expands:

\[ \Pi = \frac{k_B T}{V_0} \left[ c_1 + \frac{1}{2} (1 - 2 \chi) c_1^2 + ... \right] = \frac{N_1 k_B T}{V} + \frac{N_2}{V^2} k_B T \cdot \frac{1}{2} v_0 (1 - 2 \chi) + ... \]

Most chemists/biologists work with this part only \( \Pi_1 = M_i RT \)

Mixing vs. Phase separation

It is clear, that at large \( \chi \) the scenario might change:

\[ \Pi = \frac{k_B T}{V_0} \left[ c_1 + \frac{1}{2} (1 - 2 \chi) c_1^2 \right] \]

where \( \chi = \frac{1}{k_B T} \left[ 2 \varepsilon_{12} - \varepsilon_{11} - \varepsilon_{22} \right] \)

Positive \( \chi \) means higher repulsive \( \varepsilon_{12} \) and relatively lower repulsive (or indeed attractive \( \varepsilon_{11}, \varepsilon_{22} \)): species \{1\} and \{2\} “don’t like each other”

In the same way we can plot the mixing free energy:

\[ F_{\text{mix}} = U_{\text{mix}} - T S_{\text{mix}} = N k_B T \left( \chi \cdot c_1 (1 - c_1) + c_1 \ln c_1 + [1 - c_1] \ln [1 - c_1] \right) \]

Evidently, at large and positive \( \chi \) the mixture of two (equal-size, \( v_0 \)) species has two preferred \( \min \{F\} \) states, one rich in \{1\} the other rich in \{2\}. 
Mixing vs. Phase separation

It is tempting to try and find the minima of the mixing free energy:
\[ \frac{1}{N k_B T} \frac{\partial F_{\text{mix}}(c)}{\partial c} = \chi (1 - 2c) - \ln \left( \frac{1-c}{c} \right) = 0 \quad \Rightarrow c^* (\chi) \]

However, not only is this a bit hard – it is also not useful because the system may not be free to choose at which concentration to exist. In practice, we prepare a mixture at a given value of concentration – and then test its fate.

This is a question of stability with respect to small fluctuations!

The boundary of stability region
\[ \frac{1}{N k_B T} \frac{\partial^2 F_{\text{mix}}(c)}{\partial c^2} = -2\chi + \frac{1}{c(1-c)} = 0 \]

When the \( \chi \)-parameter is greater than: the mixture at concentration \( c \) is unstable and will have to phase-separate

\[ \chi_s = \frac{1}{2c(1-c)} \]

Phase diagram of binary mixture

Mixing free energy at different \( \chi \) (equivalent to different temperatures)

We can plot the boundaries of stability as \( \chi \) vs. \( c \), a curve which is called “spinodal line”:

In the way the Flory \( \chi \)-parameter was defined, it depends on \( T \) in the same way as the virial coefficient, but (usually) the negative of it:

\[ \chi = \frac{1}{k_B T} \left[ 2\varepsilon_{12} - \varepsilon_{11} - \varepsilon_{22} \right] \]
Phase diagram of binary mixture

Mixing free energy at different $\chi$ (equivalent to different temperatures)

The boundaries of stability ("spinodal line")

$$\chi_s = \frac{1}{2c(1-c)}$$

One can also draw the so-called "binodal line" $c^*(\chi)$, which is the position of free energy minima.

Phase transition

Prepare an equilibrium mixture at a given concentration $c_0$ – at low $\chi$ (high temperature) – and then quench it so that it ends up in the region of demixing.

How can we describe what happens?

$$\frac{F_{\text{mix}}}{Nk_BT} = \chi \cdot c(1-c) + c \ln c + [1-c] \ln[1-c]$$

Assuming the initial fluctuation of concentration $\phi$ is small, expand in series:

$$\frac{\Delta F}{Nk_BT} = \frac{2\chi c_0(1-c_0) - 1}{2c_0(1-c_0)} \cdot \phi^2 - \frac{1-2c_0}{6c_0^2(1-c_0)^2} \cdot \phi^3$$

Let us first plot this to understand the process: $\Delta F = (\chi_c - \chi) \cdot \phi^2 - b \cdot \phi^3 + c \cdot \phi^4$

$$= a(T-T_c) \cdot \phi^2 - b \cdot \phi^3 + c \cdot \phi^4$$
First order phase transition

This scenario is a typical example of the 1st order phase transition, with φ the order parameter:

\[ \Delta F = a(T - T_c) \cdot \phi^2 - b \cdot \phi^3 + c \cdot \phi^4 \]

Step 1: 
\[ \frac{\partial \Delta F}{\partial \phi} = 0: \quad \phi_0 = 0; \quad 4c \phi^2 - 3b \phi + 2a(T - T_c) = 0 \]

The non-zero solution \( \phi^* \) is the binodal line. It exists until

\[ 32ac(T - T_c) \leq 9b^2: \quad T_B = T_c + 9b^2 / 32ac \]

The "disordered" (mixed) state \( \phi = 0 \) is stable until the spinodal line is crossed, at \( T = T_c \).

Step 2: thermodynamically, the transition occurs at a point \( T = T^* \) when the free energy of the "ordered" (demixing) state becomes lower:

\[ \Delta F(\phi^*) \leq 0 \]

Hysteresis

In liquid-gas transition (e.g. from van der Waals): density fluctuation is the order parameter

Classification of phase transitions

We have just seen an example of 1st order phase transition, resulting in \( F(\phi^*) \):

The entropy: 
\[ S = -\frac{\partial F}{\partial T} \]

We can (and probably should, to practice) calculate the entropy in both the disordered (\( \phi = 0 \)) and in the ordered states. But it is clear:

Discontinuity in the 1st thermodynamic derivative of the corresponding free energy \( \rightarrow 1\)st order transition. The latent heat of transition: 
\[ L = T_c(S_2 - S_1) \]

This suggests that there might be a 2nd order transition, when the entropy is continuous, the latent heat \( L = 0 \), but a discontinuity exists in the second thermodynamic derivative, such as

\[ C = T \frac{\partial S}{\partial T} \bigg|_{T \to T_c} = -T_c \frac{\partial^2 F}{\partial T^2} \bigg|_{T \to T_c} \]

Second order phase transitions are often called critical transitions.

There is a reason for this name! Let us look one more time on the mixing phase diagram and transition
Critical point

What if our equilibrium mixture has been prepared at a concentration $c_0 = 1/2$, so that on cooling (or increasing $\chi$) it crosses the critical point?

If you look back at the series expansion of $\Delta F(\phi)$, at $c_0 = 1/2$ it becomes:

$$\frac{\Delta F}{N k_B T} = (2 - \chi) \cdot \phi^2 + \frac{4}{3} \cdot \phi^4$$

or replacing $\chi$ with $T$, it takes a generic form:

$$\Delta F = a(T - T_c) \cdot \phi^2 + b \cdot \phi^4$$

Step 1: $\frac{\partial \Delta F}{\partial \phi} = 0$: $\phi^* = \pm \frac{a(T_c - T)}{2b}$

Step 2: $\Delta F|_{\phi^*} = -\frac{a^2}{4b} (T - T_c)^2$

Entropy: $S = -\frac{\partial F(\phi^*)}{\partial T} = \frac{a^2 (T - T_c)}{2b}$

Jump: $\Delta C = T_c \frac{a^2}{2b}$

Van der Waals critical point

We have seen the expression for the free energy of interacting (dense) gas in VdW approximation:

$$F_{\text{vdW}} = -k_B T \left( \frac{1}{N!} \right) - N k_B T \ln(V - Nb) - N^2 a$$

$$= N k_B T \ln \left( \frac{N}{(V - Nb)(k_B T)^{3/2}} \right) + N k_B T \ln(\text{const}) - \frac{N^2 a}{V}$$

The critical point here is at: $T_c = 8a/27b$, $V_c = 9bN/4$

Here

$$\frac{\partial p}{\partial V}_{T_c, V_c} = 0$$

$$\frac{\partial^2 p}{\partial V^2}_{T_c, V_c} = 0$$
**Landau model of phase transitions**

Identify the proper order parameter, e.g. \( \phi \), which changes between zero in the “disordered phase” to a \((T\text{-dependent})\) value in the “ordered phase”. Assuming that at, or near the transition point \( \phi \) is small, expand the proper thermodynamic potential in power series around the disordered state \( \phi=0 \).

The linear term has to vanish, since in equilibrium \( dG/d\phi=0 \).

Near the transition only the \( \phi^2 \)-coefficient varies with \( T \) in a significant way. Symmetry of the order parameter determines if there is a \( \phi^3 \)-term.

\[
G = a(T-T_c)\cdot \phi^2 - b\cdot \phi^3 + c\cdot \phi^4
\]

**First order**

Hysteresis, jump \( \Delta \phi \) latent heat \( T\Delta S \)

**Second order \((b=0)\)**

Continuous \( \phi^* = \pm \sqrt{\frac{a(T-T_c)}{2b}} \)

---

**Ising model of ferromagnetism**

Consider a lattice with spins “up” or “down”. Without pair interaction, we know this problem well:

\[
Z_i = e^{\frac{mB}{k_B T}} + e^{\frac{-mB}{k_B T}} = 2\cosh\left(\frac{mB}{k_B T}\right)
\]

\[
M = -N m \cdot \tanh\left(\frac{mB}{k_B T}\right)
\]

If we assume that spins (dipoles \( m \cdot s_i \), where \( s_i = \pm 1 \)) actually do interact, then the pair energy with neighbours will be of the usual dipole-dipole form:

\[
E = -Bm\sum_i s_i - J\sum_{i,j} s_is_j
\]

The positive interaction constant \( J \) implies that neighbouring spins favour parallel alignment. So one expects at \( T=0 \) to have a fully aligned state with all \( s_i=1 \), but at high-\( T \) entropy should “win”

**Mean-field approximation**

Focus on a particular spin, \( s_i \), and approximate the interactions with all others by their average effect:

\[
E = -Bm\sum_i s_i - Jc\sum_i s_i\langle s \rangle
\]

Now \( Z_i = 2\cosh\left(\frac{Bn + Jc\langle s \rangle}{k_B T}\right) \)
Ising model of ferromagnetism

In the mean-field approximation we have the free energy per spin

\[ F_i = -k_B T \ln Z_i = -k_B T \ln \left[ 2 \cosh \left( \frac{B_m + J_c \langle s \rangle}{k_B T} \right) \right] \]

The closure is achieved when we recognise that the magnetisation

\[ M = m \langle s \rangle = -\left( \frac{\partial F_i}{\partial B} \right)_T = m \tanh \left( \frac{B_m + J_c \langle s \rangle}{k_B T} \right) \]

This is a bit difficult to solve, but in fact, we are mainly interested in the case when \( B=0 \), i.e. the spontaneous magnetisation. It is then easy:

\[ \langle s \rangle = \tanh \left( \frac{J_c}{k_B T} \langle s \rangle \right) \quad \Rightarrow \quad \frac{J_c}{k_B T} = 1 + \frac{1}{3} \langle s \rangle^2 \quad \text{or} \quad \langle s \rangle = \frac{3}{T} \left( T_c - T \right)^{1/2} \]

Near the critical point:

Critical exponents

One of the highest aims in physics is to find universality between different systems or phenomena.

In the study of phase transitions and critical phenomena quite a remarkable universality exists, and is reflected in the critical exponents of various parameters. The Ising model in the mean-field approximation has predicted:

\[ \langle s \rangle = \frac{3}{T} \left( T_c - T \right)^{1/2} \]

Landau theory:

\[ \phi^a = \sqrt{\frac{a}{b}} \left( T - T_c \right)^{1/2} \]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Expression</th>
<th>Exponent</th>
<th>Experiment</th>
</tr>
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<tbody>
<tr>
<td>Order parameter</td>
<td>( \phi \propto</td>
<td>T-T_c</td>
<td>^\beta )</td>
</tr>
<tr>
<td>Susceptibility</td>
<td>( \chi \propto</td>
<td>T-T_c</td>
<td>^\gamma )</td>
</tr>
<tr>
<td>Heat capacity</td>
<td>( C \propto</td>
<td>T-T_c</td>
<td>^\alpha )</td>
</tr>
<tr>
<td>Correlation of fluctuations</td>
<td>( \xi \propto</td>
<td>T-T_c</td>
<td>^\nu )</td>
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</table>
Effect of external field

Without specifying the physical nature of the system, the order parameter, or the external field, we can say in general that its effect is to contribute an additional term to the free energy:

\[ \Delta F \approx a(T - T_C) \cdot \phi^2 + b \cdot \phi^4 - h \cdot \phi \]

(If you prefer, think of the magnetic phase transition \( F(M) \) and the term \(-M \cdot B\))

It is immediately clear, from the plot and from physical standpoint, that the high-temperature state is no longer \( \phi = 0 \)

\( \frac{\partial \Delta F}{\partial \phi} = 0 : \quad 2a(T - T_C) \cdot \phi + 4b \cdot \phi^3 = h \)

Let’s not solve a cubic, just sketch what the solutions are:

\[ T > T_C \quad h > 0 \]

\[ T < T_C \]

The system is near its critical point, and with external field shifting the equilibrium value of the order parameter:

\[ \Delta F \approx a(T - T_C) \cdot \phi^2 + b \cdot \phi^4 - h \cdot \phi \]

The solution:

\[ M = Nm_0 \tanh(m_0 B / k_B T) \]

We of course have seen this in the case of paramagnetic salt (random spins in \( B \)-field)

\[ h_r = \frac{2}{3} \sqrt{\frac{2}{3}} \frac{a^{3/2} \left| T - T_C \right|^{3/2}}{b^{1/2}} \]

from

\[ \frac{\partial}{\partial \phi} \left[ 2a(T - T_C) \cdot \phi + 4b \cdot \phi^3 \right] = 0 \]
**Thermal hysteresis**

\[ \Delta F = a(T - T_c) \cdot M^2 + b \cdot M^4 - B \cdot M \]

2nd order transition loses its critical nature in an external field (high-T phase now has the same symmetry)

\[ \Delta F = a(T - T_c) \cdot \phi^2 - b \cdot \phi^3 + c \cdot \phi^4 - h \cdot \phi \]

1st order transition loses its order parameter jump and becomes continuous (after a critical point)

---

**Fluctuations**

Random motion of particles, or other elements of a system, is the source of heat energy, the “sink” where the useful energy is irreversibly dissipated into. It is also a source of thermal fluctuations of all physical parameters of this system.

Relative fluctuations in a small system could be large, however, in a very large system, relative fluctuations of macroscopic thermodynamic are very small – and we often completely ignore their effect.

There are situations when thermal fluctuations are important: in second order phase transitions, and at other critical points, fluctuations dominate the properties of the system; electric resistance is often dominated by scattering of electrons on thermal fluctuations of the lattice (phonons); scattering of light on fluctuations of density often determines the optical properties of materials.
Fluctuations

A generic microscopic method to measure a fluctuation is by evaluating its mean square:

$$\langle \Delta X^2 \rangle = \langle X^2 \rangle - \langle X \rangle^2 = \frac{1}{Z} \sum_i X_i^2 e^{-E_i/k_BT} - \left( \frac{1}{Z} \sum_i X_i e^{-E_i/k_BT} \right)^2$$

In a simple case when the energy of a microstate \{i\} depends on the variable \{X_i\} in a simple way, e.g. \(E_i/k_BT = \alpha X_i\) – the evaluation of its fluctuation is actually very easy:

$$\langle X \rangle = \frac{1}{Z} \sum_i X_i e^{-\alpha X_i} = \frac{1}{Z} \left( -\frac{\partial Z}{\partial \alpha} \right) = -\frac{\partial}{\partial \alpha} \ln Z$$

Note that:

$$\langle X^2 \rangle = \frac{1}{Z} \sum_i X_i^2 e^{-\alpha X_i} = \frac{1}{Z} \left( \frac{\partial^2 Z}{\partial \alpha^2} \right)$$

$$\frac{\partial}{\partial \alpha} \left( \frac{1}{Z} \frac{\partial Z}{\partial \alpha} \right) = \frac{1}{Z} \frac{\partial^2 Z}{\partial \alpha^2} - \frac{1}{Z^2} \left( \frac{\partial Z}{\partial \alpha} \right)^2$$

The m.s. fluctuation:

$$\langle \Delta X^2 \rangle = -\frac{\partial}{\partial \alpha} \langle X \rangle$$

Fluctuation of magnetisation

Consider a simple case of paramagnetic salt: \(N\) two-state systems with the energy \(E_i = -M_i \cdot B\)

$$\langle M \rangle = \frac{1}{Z} \sum_i M_i e^{M_i B/k_BT} = k_BT \frac{\partial Z}{\partial B} = -\frac{\partial}{\partial B} (-k_BT \ln Z)$$

As we know:

$$M = \left( \frac{\partial E}{\partial B} \right)_T$$

The m.s. fluctuation:

$$\langle \Delta M^2 \rangle = k_BT \frac{\partial \langle M \rangle}{\partial B} = \frac{k_BT}{\mu_0} \chi_M$$

As we know:

$$M = \chi_m H$$

We recall the solution for mean magnetisation of paramagnetic salt:

$$\langle M \rangle = Nm_0 \tanh \left( \frac{m_0 B}{k_BT} \right)$$

$$\langle \Delta M^2 \rangle = \frac{Nm_0^2}{\cosh^2 (m_0 B/k_BT)}$$

We are particularly interested in the magnitude of thermal fluctuations when there is no external magnetic field applied (\(B=0\)):

$$\langle \Delta M^2 \rangle_{B=0} = Nm_0^2 \rightarrow \text{relative} \quad \frac{\langle \Delta M^2 \rangle}{\langle M \rangle} \sim \frac{1}{\sqrt{N}}$$
Fluctuation of mean energy

When \( E_i = \alpha X_i \) → \[ \langle X^2 \rangle - \langle X \rangle^2 = \frac{1}{Z} \frac{\partial^2 Z}{\partial \alpha^2} - \frac{1}{Z^2} \left( \frac{\partial Z}{\partial \alpha} \right)^2 = \frac{\partial}{\partial \alpha} \left( \frac{1}{Z} \frac{\partial Z}{\partial \alpha} \right) \]

Using the same approach, let us briefly look at the fluctuation of mean energy:

\[ U = \frac{1}{Z} \sum_i E_i e^{-E_i/k_BT} = -\frac{\partial}{\partial \beta} \ln Z \]

The m.s. fluctuation is, therefore:

\[ \langle \Delta U^2 \rangle = \frac{\partial}{\partial \beta} \left( \frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) = k_B T \left( \frac{\partial U}{\partial T} \right) \]

We recall what the derivative \( dU/dT \) is (at least when evaluated at \( V=\text{const} \)). For an ideal gas, where we know all the answers:

\[ U = \frac{3}{2} Nk_B T \; ; \; C_v = \frac{3}{2} Nk_B \]

\[ \frac{\sqrt{\langle \Delta U^2 \rangle}}{U} = \frac{\sqrt{2/3}}{N^{1/2}} \]

Connection with thermodynamics

Let us consider our system in contact with a large reservoir. Earlier in the course we have identified the probability \( P(X) \) for the system to have a certain value of its variable.

If \( U_{\text{tot}} \) is the energy of system+reservoir, and \( \Omega_{\text{tot}}(X, U_{\text{tot}}) \) is the number of microstates of system+reservoir (with a fixed value of system’s \( X \)), then:

\[ S_{\text{tot}}(X, U_{\text{tot}}) = k_B \ln \Omega(X, U_{\text{tot}}) \quad \text{and} \quad P(X) \propto \Omega(X, U_{\text{tot}}) \propto e^{S_{\text{tot}}(X, U_{\text{tot}})/k_B} \]

Earlier we have dealt with the difficult problem of system+reservoir by introducing the availability \( dA = -T_R dS_{\text{tot}} \)

\[ P(X) \propto e^{-A(X)/k_BT} \]

For a large system \( P(X) \) is “almost Gaussian”, so let us expand its exponent about the point \( X=X_{eq} \), when the fluctuation \( \Delta X = X-X_{eq} \) is small:

\[ A(X) = A(X_{eq}) + (X - X_{eq}) \left[ \frac{\partial A}{\partial X}_{X=eq} \right] + \frac{1}{2} (X - X_{eq})^2 \left[ \frac{\partial^2 A}{\partial X^2} \right]_{X=eq} \]

\[ P(\Delta X) = \frac{1}{\sqrt{2\pi \langle \Delta X^2 \rangle}} \exp \left[ -\frac{(X - X_{eq})^2}{2\langle \Delta X^2 \rangle} \right] \]

where \( \langle \Delta X^2 \rangle = \frac{k_BT}{\left( \frac{\partial^2 A}{\partial X^2} \right)_{X=eq}} \)
Connection with thermodynamics

We have dealt with the difficult problem of availability by noting how for certain thermodynamic constraints it reduces to a natural T.D. potential of our system.

For instance, for a system at fixed \((V, N)\):

\[
A(X) - A(X_{eq}) = dF = \frac{1}{2} \frac{\partial^2 F}{\partial X^2} (X - X_{eq})^2
\]

\[
P(\Delta X) \propto \exp \left[ -\frac{1}{2k_B T} \frac{\partial^2 F}{\partial X^2} \right] (X - X_{eq})^2 ; \text{ so } \langle \Delta X^2 \rangle = k_B T \frac{\partial^2 F}{\partial X^2} \bigg|_{eq}
\]

… or similar with a correspondingly different T.D. potential if other conditions are imposed on the system in question.

Fluctuations and Linear response

We have found that for any thermodynamic parameter, its small fluctuations about the equilibrium are described by the second derivative of an appropriate potential:

\[
\langle \Delta X^2 \rangle = k_B T \frac{\partial^2 F}{\partial X^2} \bigg|_{eq}
\]

The linear response coefficient is connecting the “force” and the “displacement”:

\[
Y = \kappa X
\]

linear response : \( \langle \Delta X^2 \rangle = k_B T \frac{\partial^2 \frac{\Delta X}{\Delta Y} |_{eq}}{\kappa} \)

<table>
<thead>
<tr>
<th>Variable (X)</th>
<th>Conjugate force (Y)</th>
<th>Linear response coeff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>displacement (x)</td>
<td>force (f)</td>
<td>spring constant (\kappa)</td>
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<tr>
<td>pressure (p)</td>
<td>volume (V)</td>
<td>compressibility (\beta)</td>
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<tr>
<td>temperature (T)</td>
<td>entropy (S)</td>
<td>heat capacity (C)</td>
</tr>
<tr>
<td>magnetisation (M)</td>
<td>magn.field (B)</td>
<td>susceptibility (\chi)</td>
</tr>
</tbody>
</table>
Fluctuations near critical points

Let's recall the form of the free energy near a critical point:

\[ \Delta F \approx a(T - T_c) \cdot \phi^2 + b \cdot \phi^4 - h \cdot \phi \]

If you prefer, think of the ferromagnet in the mean-field approximation, then \( \phi = M \), in the external field, \( h = B \)

In general, the m.s. fluctuation of the order parameter is

\[ \langle \Delta \phi^2 \rangle = \frac{k_B T}{2a(T - T_c) + 12b \cdot \phi^2} \]  

\( \phi^* \) = \( \phi \) in the external field

\[ \chi = \mu_0 \left( \frac{\partial M}{\partial B} \right) = \frac{k_B}{k_B T} \langle \Delta M^2 \rangle \]

Without external field:

At \( T > T_C \)  \( \phi^* = 0 \) :  \[ \langle \Delta \phi^2 \rangle = \frac{k_B T}{2a(T - T_c)} = k_B T \left( \frac{\partial \phi}{\partial h} \right)_{h=0} \]

At \( T < T_C \)  \( \phi^* = \sqrt{-\frac{a(T - T_c)}{2b}} \) :  \[ \langle \Delta \phi^2 \rangle = - \frac{k_B T}{4a(T - T_c)} = \frac{k_B T}{4a(T - T_c)} \]

With external field present:

At \( T > T_C \)  \( \phi^* = \frac{h}{2a(T - T_c)} \) :  \[ \langle \Delta \phi^2 \rangle = k_B T \left( \frac{\partial^2 \phi}{\partial h^2} \right)_{h=0} \]

At all \( T \)  \( \phi^* (T, h) \) :  \[ \langle \Delta \phi^2 \rangle = \frac{k_B T}{\text{function}(T, h)} \]

\[ \chi_{\mu} \sim \langle \Delta M^2 \rangle \]
Microscopic origin of fluctuations

The origin of fluctuations of all thermodynamic quantities is, of course, the random thermal motion of particles in the medium (the energy of which we called “heat”). Fluctuations are an essential element of Nature, since they are the mechanism by which the system explores its available phase space; the statistical summation of quantities such as partition function requires this to achieve equilibrium.

On the other hand, thermal fluctuations make the value of any system parameter, or the dynamical trajectory of a particle, uncertain. No individual observation has any value, only the probabilities and the averages do.

We now study the Brownian motion, which is the simplest and most transparent effect that allows us to explore microscopic origins of thermal fluctuations. The classical experiments of Robert Brown tracked the motion of small (1µm) particles in water.

Brownian motion

The free particles should move according to the dynamical equation

\[ m \frac{dv}{dt} = -\gamma v \]

where the friction drag coefficient \(\gamma\) for a sphere of radius \(a\) in a fluid of viscosity \(\eta\) has the Stokes’ form: \(\gamma = 6\pi \eta a\).

Movement in a viscous fluid is dissipative, so if a particle starts with a velocity \(v_0\), that will decay as

\[ v = v_0 e^{-\gamma/m t} \]

Yet Robert Brown has recorded particles moving continuously, following a random-walk trajectory:

This type of motion is called stochastic. It clearly requires an additional force to act on the particle, which we shall call the stochastic force \(\zeta(t)\) (sometimes it is called the random noise).
**Stochastic force**

The dynamical equation of free particle changes into:

$$m \frac{dv}{dt} = -\gamma v + \xi(t)$$

where the stochastic force may have a typical time-dependence (in a 1D projection):

If we zoom in, there is a characteristic time scale between collisions of our particle with molecules of water, which are in thermal motion. Let us finish by defining the statistical characteristics of such a stochastic force:

It is pretty clear that: $$\langle \xi(t) \rangle = 0$$ but $$\langle \xi(t)^2 \rangle = \text{const}$$

This is the definition of "white noise", complete lack of correlation between different pulses!

**Langevin equation**

The stochastic equation has a generic form: start with the dynamical equation (generic Newton’s) and add the stochastic force to all other forces present. Even for a free particle we must include friction, to provide the sink for the energy delivered by the collisions.

The general solution:

$$v(t) = v_0 e^{-(\gamma/m) t} + \int_0^t e^{-(\gamma/m)(t-t')} \frac{1}{m} \xi(t') dt'$$

Either work out the solution from the Green function of the corresponding homogeneous equation – or just check it by direct differentiation.

As with the stochastic force itself, there is no meaning in the value of the (also stochastic) particle velocity $$v(t)$$. Only the averages make sense. Clearly $$\langle v(t) \rangle = 0$$.
Mean square velocity

The general solution:

\[ v(t) = v_0 e^{-\gamma/m}t + \int_0^t e^{-\gamma/m}[t-t'] \frac{1}{m} \xi(t')dt' \]

\[ v^2 = v_0^2 e^{-2\gamma/m}t + 2v_0 e^{-\gamma/m}t \int_0^t e^{-\gamma/m}[t-t'] \frac{1}{m} \xi(t')dt' + \int_0^t e^{-\gamma/m}[t-t'] v_0 e^{-\gamma/m}[t-t'] \frac{1}{m^2} \xi(t_1) \xi(t_2)dt_1 dt_2 \]

Taking the average:

\[ \langle v^2 \rangle = v_0^2 e^{-2\gamma/m}t + \int_0^t e^{-\gamma/m}[t-t'] \frac{1}{m} \xi(t')dt' \]

\[ \langle v^2 \rangle = v_0^2 e^{-2\gamma/m}t + \frac{\Gamma}{m^2} \int_0^t e^{-2\gamma/m}[t-t'] dt_1 \]

\[ \langle v^2 \rangle = v_0^2 e^{-2\gamma/m}t + \frac{\Gamma}{2m\gamma}(1 - e^{-2\gamma/m}t) \]

Maxwell distribution of the velocity gives:

\[ \langle v^2 \rangle = \int_{-\infty}^{\infty} \frac{d\xi}{\sqrt{2\pi\gamma}} e^{-\gamma/\xi^2} = \frac{\Gamma}{2m\gamma} \]

\[ \Gamma = 2k_B T \cdot \gamma \]

Decay of the initial condition

\[ \langle v^2 \rangle = \frac{1}{2mT} \]

Mean square velocity

The mean kinetic energy:

\[ \langle m v^2 \rangle = \frac{m}{2} \left( \int_0^t e^{-\gamma/m}[t-t'] \frac{\xi(t')}{m} d\tau \right)^2 \]

As before, the only object that needs “averaging” is \( \xi(t) \) under the integral:

\[ = \int_0^t \int_0^t e^{-\gamma/m}[t-t'] e^{-\gamma/m}[t-t'] \left( \langle \xi(t_1) \xi(t_2) \rangle \right) d\tau_1 d\tau_2 \]

Long times: steady-state mean K.E.

\[ = \frac{\Gamma}{2m} \int_0^\infty e^{-2\gamma/m}[t-t] d\tau_1 = \frac{\Gamma}{4\gamma} = \frac{1}{2} k_B T \]

The important result we just found says that the mean-square intensity of the random force \( \Gamma \) is proportional to temperature \( k_B T \) (that’s expected) but also the dissipative friction constant \( \gamma \)!

This is one of many forms of Fluctuation-Dissipation Theorem
**Fluctuation-Dissipation relationship**

Intensity of the random noise (thermal motion of molecules): the energy supplied to the particle

\[ \langle \xi^2 \rangle \propto \Gamma \]

Dissipation of energy of the particle due to the friction drag against the same medium

\[ \gamma = 6\pi \eta a \]

The Langevin equation has the underlying relaxation dynamics, with the characteristic time of velocity decay

\[ \tau_v = m / \gamma \]

\[ m \frac{dv}{dt} = -\gamma v + \xi(t) \]

The equilibrium (Maxwell) distribution of velocities in the ensemble of such particles is established after this time scale.

---

**Overdamped limit**

But if our “observation window” is much wider than the velocity relaxation time (1\(\mu\)m particles in water: \(m/\gamma \sim 2 \cdot 10^{-8} s\)), then the particle effectively has no acceleration, and we are left with the balance of forces, viscous and stochastic:

\[ 0 = -\gamma v + \xi(t) \quad \text{or} \quad \frac{dx}{dt} = \frac{1}{\gamma} \xi(t) \]

Which we can easily solve to produce the expression

\[ x(t) = \frac{1}{\gamma} \int_0^t \xi(\tau) d\tau \]

The stochastic expression for the particle position \(x(t)\) is useless!

We can, however, build other quantities which can be evaluated and studied. For example, the mean square displacement:

\[ \langle x(t)^2 \rangle = \frac{1}{\gamma^2} \int_0^t \int_0^t \langle \xi(\tau_1) \xi(\tau_2) \rangle d\tau_1 d\tau_2 \]
Mean square displacement

As before, averaging under the integral: \( \langle \xi(t_1)\xi(t_2) \rangle = \Gamma \delta(t_1 - t_2) \)

\[
\langle x(t)^2 \rangle = \frac{1}{\gamma^2} \int_0^t \Gamma \, d\tau = \left( \frac{\Gamma}{\gamma^2} \right) t \Rightarrow 2D t
\]

This represents diffusion, and defines the diffusion constant \( D \)

The F.D. relationship: \( \Gamma = 2k_B T \cdot \gamma \)

Gives the Einstein relation between the diffusion constant of a particle, and its kinetic friction:

\[
D = \frac{k_B T}{\gamma}
\]

For a spherical particle with the Stokes form of the friction drag

\[
D = \frac{k_B T}{6\pi \eta a}
\]

Diffusion and probability

We are looking at the processes, whose nature is inherently uncertain – all one can detect (with crude devices) is some average properties. But averaging implies that there is some probability distribution: \( P(x(t)) \) for the variable \( x(t) \).

Just like we had earlier, in thermodynamics: \( P(x) \sim e^{-E(x)/kT} \)

What factors contribute to the probability that would lead to the diffusive motion?

\[
\bar{x} = \sqrt{\langle x(t)^2 \rangle} = \sqrt{2D \cdot t}
\]

Slow, compared with steady motion, or acceleration:

\[
\bar{x} = v_0 \cdot t
\]

\[
\bar{x} = \frac{1}{2} a \cdot t^2
\]
Random walk

Let us consider the simple example of free diffusive motion along one axis, the variable \( x(t) \), as a sequence of random steps: to the left and to the right:

Steps of length \( a \) occur at time intervals \( \Delta t \). The total of \( N \) steps is made: \( t = N \cdot \Delta t \).

The total displacement after \( N \) steps is \( x(t) \), but the total length traveled is \( L = N \cdot a \).

If we count the number of steps to the right, \( N_{+} \), and to the left, \( N_{-} = N - N_{+} \), then we can find the probability \( P(x) \) as that of making \( N_{+} \) steps out of the total of \( N \) — in any order!

\[
P(N_{+}, N) = \left( \frac{1}{2} \right)^{N} \frac{N!}{N_{+}! (N - N_{+})!} \]

Use the Stirling formula, as always:

\[
N! \approx e^{N \ln N - N}
\]

Where we named the constant:

\[
D = \frac{a^{2}}{2\Delta t}
\]

Random walk = Diffusion

The sequence of \( \pm \) steps along one axis is an example of diffusive motion!

Steps of length \( a \) occur at time intervals \( \Delta t \).

The average displacement \( \langle x(t) \rangle = 0 \), of course. But the mean square displacement is determined by the Gaussian probability \( P(x) \) as the variance:

\[
\langle x^{2} \rangle = \int x^{2} P(x) \, dx = \int \frac{x^{2} e^{-x^{2}/4D \Delta t}}{\int e^{-x^{2}/4D \Delta t} \, dx} \, dx = 2D \cdot t
\]

Compare the Einstein relation for the diffusion constant, with our “counting states” result: dividing the elementary step length by the time to make this step

\[
D = k_{B} T / \gamma = \frac{a^{2}}{2\Delta t}
\]
Probability of random walk

Just as a simple oscillator, the ideal gas, or the dissipative friction – the random walk is a model that applies to great many situations!

If the event \( a \) has values of opposite sign, and happens many times, the probability to have a certain net amount \( x=(N_+ - N_-)a \) is given by

\[
P(x, t) \approx e^{-\frac{x^2}{2a^2N}} \quad \text{or} \quad e^{-\frac{x^2}{4Dt}}
\]

Where the total “time” is \( t=(N_+ + N_-)\Delta t \) and the “diffusion constant” \( D=\frac{1}{2a^2} \).

Free diffusion equation

The sequence of \( \pm \) steps along one axis.

The transition probability of making a step from the position \( k \) to \( (k+1) \) is \( w(k,k+1)=1/2 \). Obviously, \( w(k,k-1)=1/2 \) too. Now, the probability to end up in a position \( k \) after \( N+1 \) steps is made of two parts:

\[
P(k, N+1) = w(k-1,k) \cdot P(k-1,N) + w(k+1,k) \cdot P(k+1,N)
\]

Subtract \( P(k,N) \) from both sides, and use the fact that \( w(k-1,k)+w(k+1,k)=1 \)

\[
P(k, N+1) - P(k,N) = \frac{\partial P(k,t)}{\partial t}
\]

\[
\frac{\Delta t}{2}[P(k-1,N) - 2P(k,N) + P(k+1,N)] = \frac{1}{2\Delta t} \frac{\partial^2 P(k,t)}{\partial k^2} = \frac{a^2}{2\Delta t} \frac{\partial^2 P(x,t)}{\partial x^2}
\]

Diffusion equation:

\[
\frac{\partial P(x,t)}{\partial t} = \left( \frac{a^2}{2\Delta t} \right) \frac{\partial^2 P(x,t)}{\partial x^2}
\]
Diffusion equation

This, as the random walk, is completely generic to the stochastic system that has equal $\pm \frac{1}{2}$ probabilities of a step.

If you recall that $P(x,t)$ represents the concentration $c(x,t)$ (or density) of particles, then we realize that empirically this relation has been known long ago: Fick (1885) empirically described mass diffusion by assuming that the flux of particles is proportional to the gradient of concentration:

$$J = -D \frac{d c(x,t)}{dx}$$

Conservation of mass implies the continuity relation: to increase $c(x,t)$ you need “influx”

$$\frac{d c(x,t)}{dt} = \frac{d J(x,t)}{dx}$$

Also, notice a remarkable analogy between the free diffusion and the Schrödinger equation for a free quantum particle:

Not surprisingly, the early quantum theory was considering ideas of “imaginary time”, or an effective imaginary diffusion constant: $D = \frac{i\hbar}{2m}$

Free particle in a box

If the particle is confined to a certain range of space, say $(0-L)$, then the probability to find it evolves with time.

Taking into account the normalization of probability (or, equivalently, the constant mass of many particles in this box).

$$P(x,t) = \frac{1}{\sqrt{4\pi D t}} e^{-x^2/4Dt}$$

Recall the diffusion constant: $D = k_B T/\gamma$

Thermal motion (fluctuations) make any exact prediction of a measurement outcome impossible, in a different way but with the similar outcome to quantum effects.
Confined Brownian motion

Let us now look how the thermal noise affects the system with a potential energy, using the examples of a particle on a spring

Previously the free particle "started" with a velocity $v_0$ and no reference position in space. After a characteristic time $\tau = (m/\gamma)$ the initial velocity is "forgotten" and the Maxwell distr. $P(v)$ is established. But there is still no reference position in space, and the diffusion continuously spreads the particle "envelope": $\langle x^2 \rangle = 2Dt$

When the particle is confined by the potential $U=\frac{1}{2} \alpha x^2$ around the equilibrium at $x=0$, the situation changes.

The overdamped Langevin eq.

$x(t) = x_0 e^{-(\alpha/\gamma)t} + \int_0^t e^{-(\alpha/\gamma)(t-t')} \frac{1}{\gamma} \xi(t') dt'$

The solution is obvious, from the analogy with the earlier free Langevin eq. for the velocity!

Particle in a potential well

First of all, there is now a new time scale in the problem, $\tau = \gamma/\alpha$, which determines how long does it take for the particle to "forget" its initial position and adopt the equilibrium distribution.

$x(t) = x_0 e^{-(\alpha/\gamma)t} + \int_0^t e^{-(\alpha/\gamma)(t-t')} \frac{1}{\gamma} \xi(t') dt'$

Finding the m.s. $\langle x^2 \rangle$ follows the same steps as we made in the evaluation of the m.s. $\langle v^2 \rangle$

$\langle x^2 \rangle = x_0^2 e^{-2(\alpha/\gamma)t} + \int_0^t \int_0^t e^{-(\alpha/\gamma)(t-t')} e^{-(\alpha/\gamma)(t''-t')} \frac{1}{\gamma^2} \langle \xi(t) \xi(t'') \rangle dt' \cdot dt''$

$\langle x^2 \rangle = x_0^2 e^{-2(\alpha/\gamma)t} + \frac{\Gamma}{2\alpha \gamma} (1-e^{-2(\alpha/\gamma)t})$

After the time $t \gg \tau_x$

$\langle x^2 \rangle = \frac{\Gamma}{2\alpha \gamma} = \frac{k_BT}{\alpha}$

We have seen this very recently!

The m.s. deviation of $x$ from zero is the m.s. fluctuation about the equilibrium. $\langle x^2 \rangle$ then is given by our general relation:

$\langle \Delta x^2 \rangle = k_BT \left| \frac{\partial x}{\partial Y} \right|_{eq}$

Here the force conjugate to the displacement $x$ is just the spring force $f = \alpha x$
**Diffusion and drift**

Consider our earlier scheme of deriving the free diffusion equation from analysing the probabilities of ± steps, with transition probabilities $w_{±} = ½$.

Let us now consider a constant bias:

$$w(k,k+1) = 1/2 + ε \text{ and } w(k,k-1) = 1/2 - ε.$$  

Starting from the balance:

$$P(k, N+1) = w(k-1,k) \cdot P(k-1,N) + w(k+1,k) \cdot P(k+1,N)$$

subtracting $P(k,N)$ from both sides, and forming the discrete derivatives:

$$\frac{P(k, N+1) - P(k, N)}{\Delta t} = \frac{\partial P(k, t)}{\partial t} = \frac{1}{2\Delta t} \frac{\partial^2 P(k, t)}{\partial k^2} + \frac{2 \varepsilon}{\Delta t} \frac{\partial P(k, t)}{\partial k}$$

Diffusion with a constant drift:

$$\frac{\partial P(x, t)}{\partial t} = \left( \frac{a^2}{2\Delta t} \right) \frac{\partial^2 P(x, t)}{\partial x^2} + \left( \frac{2a \varepsilon}{\Delta t} \right) \frac{\partial P(x, t)}{\partial x}$$

**Diffusion in external potentials**

With a constant drift “force” the diffusion equation adopts a modified form. There is a general solution of this, but let us look at the steady state - the equilibrium distribution.

$$0 = D \frac{\partial^2 P_{eq}(x)}{\partial x^2} + C \frac{\partial P_{eq}(x)}{\partial x} + \frac{C}{D} P_{eq}(x)$$

$$P_{eq} = P_0 e^{-C/D}$$

Example: Sedimentation by gravity: $V=mgz$, force $f=-mg$  

$$P_{eq} = P_0 e^{-mgz/\gamma}$$

which will follow if we take $C=mg/\gamma$.

This suggests that a general diffusion equation of motion in an arbitrary external potential $V(x)$ would take the form

$$\frac{\partial P(x, t)}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial P(x, t)}{\partial x} - \left( \text{force} \over \gamma \right) P(x,t) \right) = \frac{\partial}{\partial x} \left( D \frac{\partial P(x, t)}{\partial x} + \frac{1}{\gamma} \frac{\partial V}{\partial x} P(x,t) \right)$$

In different sources this modified diffusion equation is often called the Fokker-Planck equation. However, strictly speaking, the F-P equation is for the joint probability $P(v,x,t)$ – whereas this reduced form has the name of **Smoluchowski equation** (1906).
Flux of probability

We now see how the equilibrium distribution arises as the limiting \((t \to \infty)\) steady state of generalised diffusion:

\[
\frac{\partial P_{eq}}{\partial P} = -\frac{1}{\gamma D} \frac{\partial V}{\partial x} \, dx
\]

\[
P_{eq} = P_0 e^{-\frac{V(x)}{k_B T}}
\]

The probability distribution \(P(x,t)\) is a continuous field with a fixed normalisation. As all such fields, it must satisfy the continuity relation, which states:

\[
\frac{\partial P(x,t)}{\partial t} = -\text{div} [\text{FLUX}(x,t)]
\]

Here the flux of probability \(J(x,t)\) has to be defined as:

\[
\frac{\partial P(x,t)}{\partial t} = -\frac{\partial J(x,t)}{\partial x}
\]

\[
J(x,t) = -D \frac{\partial P(x,t)}{\partial x} + \left( \frac{1}{\gamma} \right) P(x,t) = -D e^{-\beta V(x)} \frac{\partial}{\partial x} [e^{\beta V(x)} P(x,t)]
\]

For the force-free diffusion, the flux of probability (which is equivalent to the flux of Brownian particle concentration in a solution) is given by the classical gradient of concentration:

\[
J = -D \cdot \nabla c(x,t)
\]

Escape over potential barriers

Consider a system in a metastable state, separated by a potential barrier \(\Delta\) from reaching its thermodynamical equilibrium. The generic question is:

How long would it have to “wait” for a sufficiently large thermal fluctuation to take it over the barrier?

The classical Kramers problem: let us look at the steady-state current of particles from \(A\) to \(B\). The constant flux is given by

\[
J = -D e^{-\beta V(x)} \frac{\partial}{\partial x} [e^{\beta V(x)} P(x)]
\]

Integrate both sides between \(A\) and \(B\):

\[
J \cdot \int_A^B e^{\beta V(x)} \, ds = -D \left[ e^{\beta V(x)} P(x) \right]_A^B
\]

If the potential well at \(B\) is deep

\[
J \cdot \int_A^B e^{\beta V(x)} \, ds = +D \cdot P(x_A)
\]

Assuming the basic shape of potential barrier:

\[
V(x) = \Delta - \frac{1}{2} \kappa_C (x-x_0)^2
\]

the integral gives the approximate steepest-descent result:

\[
J \cdot \left( e^{\beta V(x)} \int_A^B e^{-\Delta \kappa_C (x-x_0)^2} \, ds \right) = J \cdot \left( e^{\beta V(x)} \sqrt{\frac{4\pi \kappa_C}{\kappa_C}} \right) = +D \cdot P(x_A)
\]
Escape over potential barriers

We have obtained the steady-state flux to carry our system from $A$ to $B$ (over the energy barrier towards its true equilibrium):

$$J = D e^{-\left(\frac{\kappa}{4\pi k_B T}\right)} \frac{\kappa \kappa}{4\pi k_B T} \cdot P(x_A)$$

The rate of this escape (i.e. the inverse life-time at $A$) is by definition the ratio of the flux to the number of particles present at $A$, which in turn is given by

$$dN_A = P(x_A) e^{-\beta V_A} \cdot dx: \quad N_A = P(x_A) \int_{-\infty}^{\infty} e^{-\frac{\kappa x^2}{4\pi}} \cdot dx = \frac{4\pi k_B T}{\kappa_A}$$

The rate of escape over the barrier $\Delta$:

$$\frac{1}{\tau} = \frac{J}{N_A} = \frac{D}{4\pi k_B T} \sqrt{\kappa_A \kappa_C} \cdot e^{-\left(\frac{\kappa}{4\pi\gamma}\right)} = \sqrt{\kappa_A \kappa_C} \cdot e^{-\left(\frac{\kappa}{4\pi\gamma}\right)}$$

This is a very important (and famous) result explaining the so-called Arrhenius law, empirically relating the life time of any metastable state to the Boltzmann exponential with the energy barrier (found anywhere from biology/chemistry to mechanical engineering).

**SUMMARY**

- **Analytical Thermodynamics**
  - Variables and Tools to evaluate observable quantities, "starting from any position"
  - Pairs of conjugate variables, Potentials & proper variables, Three "tools" of evaluation, Thermodynamic equilibrium
- **Foundations of Statistical Physics**
  - Basic model systems, Classical ideal gas Quantum "ideal" gases
  - Ensembles & Partition functions, Phase space, Connection to Thermodynamics
- **Interacting systems, phases**
  - Pair interactions, van der Waals, 2nd virial coefficient, phase transitions
  - Mixing & phase separation, 1st vs. 2nd order transitions, critical exponents
- **Fluctuations**
  - Thermodynamics of fluctuations, Microscopic mechanism of fluctuations
  - M.S. fluctuation via probability, F.D.Theorem, Brownian motion & diffusion eqs
End of the 18-lecture material

...do we want an extra “Finale”?

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**Transition probability**

Let us say, the free particle travels from A to B in the time \( t \).

The path may be long and arduous, but if we break it in a sequence of very short steps, then each step is a straight “jump” \( x_k \rightarrow x_{k+1} \).

Probability of this jump, taking the time \( \Delta t \), is:

\[
P_k = \frac{1}{{\sqrt {4\pi D \cdot \Delta t} }} e^{-\frac{(x_{k+1} - x_k)^2}{4D \cdot \Delta t}}
\]

Probability to get all the way from A to B is:

\[
P(A \rightarrow B) = \prod_{k=1}^{N} P_k = \left( \frac{1}{{\sqrt {4\pi D \cdot \Delta t} }} \right)^N \exp \left[ -\frac{1}{4D \cdot \Delta t} \sum_{k=1}^{N} (x_{k+1} - x_k)^2 \right]
\]

\[
P(A \rightarrow B) = \text{const} \cdot \exp \left[ -\frac{1}{4D} \int_0^t \left( \frac{dx}{dt} \right)^2 dt \right]
\]

Recall the diffusion constant:

\[
D = k_B T / \gamma
\]

\[
P(A \rightarrow B) = \text{const} \cdot \exp \left[ -\frac{\gamma}{2mk_B T} \int_0^t \left( \frac{mv^2}{2} \right) dt \right]
\]
Action

If we generalize, the conclusion is that the probability to get from A to B under the inevitable effect of thermal fluctuations is controlled by the value of

\[ -\frac{\gamma}{2mk_B T} \cdot S[x(t), v(t)] \]

where

\[ S = \int_0^t \left( \frac{mv^2}{2} \right) dt \]

is called the Action.

The Action is not a function of time, or position: it is a function of, and so describes the whole trajectory of the particle (or the evolution of a more general system).

We conclude that the highest probability will be for the path (the sequence of small steps \( x_k(t) \) along the way), which has the minimal Action. So far this was for the free particle, with no potential energy acting on it.

Minimal Action

The Action in the presence of potential energy has the form:

\[ S = \int_0^t \left( \frac{mv^2}{2} - V(x) \right) dt \]

It remains the fundamental property of any physical system in the classical regime, that the highest probability of its evolution will be for the path of Minimal Action. This is the definition of “equilibrium path” – something that we find in dynamics.

\[ P_{A \rightarrow B} \propto \exp\left[-\frac{\gamma}{2mk_B T} \cdot S[x(t)]\right] \]

How tightly the system is confined to stay on this equilibrium path of evolution, \( \min[S] \), is determined by the constants:

\[ \min\left[-\frac{\gamma}{2mk_B T} \cdot S\right] \]