We discuss mean-free path, random walks and Brownian motion. Perhaps, \* indicates some possible discussions.

1 [Mean free path and diffusion]
Consider a (ideal gas) mixture consisting of two chemically distinct species A and B. The number density of chemical species A (resp., chemical species B) is \(n_A\) (resp., \(n_B\)), the diameter of particle A (resp., particle B) is \(d_A\) (resp., \(d_B\)) and its mass is \(m_A\) (resp., \(m_B\)).

(1) Using the simple idea of the swept volume (Fig. 6.1), calculate the mean free path for A moving through the gas of B (i.e., \(n_A = 0\)):

(i) Get the cross section \(\sigma_{AB}\) of the cylinder: the cross section \(\sigma_{AB}\) of the cylinder (the swept volume by A colliding with B) can be written in terms of \(d_A\) and \(d_B\).

(ii) The number of B particles in this swept volume should be the number of collisions experienced by a single A with B. This tells you how to compute the mean free path \(\ell_{AB}\) of particle A in gas B under the assumption that B molecules are not moving.

(iii) How can you take the motion of B into account (approximately; cf. (6.1) → (6.2))?
We need the relative speed: the relative speed is, on the average, the average relative speed of particle A and B that can be estimated as (5.74), where \(m\) should be the reduced mass \(\mu\) (you must write it in terms of \(m_A\) and \(m_B\)).

(2) What is the diffusion constant (correctly speaking, it is called the mutual diffusion constant \(D_{AB}\)) of minority A through majority B? Use our elementary result (6.28).

(3) Suppose B is shear minority and diffusing through the A gas. What is \(D_{BA}\)?

(4) We imagine a particle of A is running and hitting B. Using the results of (i) - (iii) in (1), estimate the total number \(Z_{AB}\) of collisions per unit time that occur between particles A and B in a unit volume.

(5)* Obtain \(Z_{AA}\), the number of collisions among A’s in a unit volume per unit time.

(6)* Can you obtain \(D_{AA}\) (the so-called self-diffusion constant)? Is it a physical quantity?

**Soln.**

(1)

(i) Particles A and B can collide, if their centers of mass is within distance \((d_A + d_B)/2\), so the collision cross section is given by

\[
\sigma_{AB} = \frac{\pi}{4}(d_A + d_B)^2. \tag{DH4.1}
\]

(ii) The condition must be

\[
\sigma_{AB} \times \ell_{AB} \times n_B = 1
\]

or

\[
\ell_{AB} = \frac{1}{\sigma_{AB}n_B} = \frac{1}{\frac{\pi((d_A + d_B)/2)^2n_B}}. \tag{DH4.3}
\]

(iii) If B molecules are also moving, we must reduce (DH4.3) with the ratio of the relative
speed of A and B and the speed of A. (5.74) tells us the mean relative speed $v_{AB}$ must be

$$v_{AB} = \sqrt{\frac{8k_BT}{\pi\mu}} = \sqrt{\frac{8(m_A + m_B)k_BT}{\pi m_A m_B}}. \quad (DH4.4)$$

The latter is just (5.74) with $m = m_A$, so the ratio must be $\sqrt{(m_A + m_B)/m_B}$. Thus we get

$$\ell_{AB} = \frac{1}{\sigma_{AB} n_B} \sqrt{\frac{m_B}{m_A + m_B}} = \frac{\sqrt{m_B}}{\pi (d_A + d_B)/2^2 \sqrt{(m_A + m_B)n_B}}. \quad (DH4.5)$$

This indeed gives our formula (6.2), if A and B are identical.

(2) In (6.28) $\overline{v}$ is the speed of A and $\ell$ must be $\ell_{AB}$. Therefore,

$$D_{AB} = \frac{1}{3} \frac{1}{\pi [(d_A + d_B)/2]^2 n_B} \sqrt{\frac{8k_BT}{\pi m_A}}. \quad (DH4.6)$$

Here the numerical factor $2\sqrt{2}/3 \approx 1$ should not be paid much attention (so ignored below).

(3) By symmetry, we get

$$D_{BA} = \frac{1}{\pi [(d_A + d_B)/2]^2 n_A} \sqrt{\frac{k_BT}{\pi m_B}}. \quad (DH4.7)$$

(4) To count the number $z_{AB}$ of collisions between a particular particle of A and B particles in one second, we can imagine a ‘swept cylinder’ of cross section $\sigma_{AB}$ times length $v_{AB}$ (see (DH4.4)) and then count all B particles in it:

$$z_{AB} = \pi \left[\frac{d_A + d_B}{2}\right]^2 \sqrt{\frac{8(m_A + m_B)k_BT}{\pi m_A m_B}} n_B. \quad (DH4.8)$$

This is for one particle of A and there are $n_A$ in a unit volume, so

$$Z_{AB} = n_A z_{AB} = \pi \left[\frac{d_A + d_B}{2}\right]^2 \sqrt{\frac{8(m_A + m_B)k_BT}{\pi m_A m_B}} n_A n_B. \quad (DH4.9)$$

Notice that this is symmetric as you expect $Z_{AB} = Z_{BA}$.

(5) Perhaps, you may think equating quantities with suffix A and those with B suffices by replacing B → A. Wrong, because A particles are indistinguishable. In the case of A and B, a collision due to A coming from ‘right’ and B coming from ‘left’ and that due to B coming from ‘right’ and A coming from ‘left’ are distinct. If B is A, then these two collisions are identical, so (DH4.9) with A = B double-counts the number of AA-collisions. Therefore,\(^1\)

$$Z_{AA} = \frac{1}{2} \pi d_A^2 \sqrt{\frac{8k_BT}{\pi m_A}} n_A^2 = \pi d_A^2 \sqrt{\frac{2k_BT}{\pi m_A}} n_A^2 \quad (DH4.10)$$

\(^1\)Although I said the numerical prefactor is not important, IF you use the same approximations, the overall multiplier 1/2 in the result must be respected.
(6) Strictly speaking, the particle ‘self-diffusion’ coefficient $D_{AA}$ is meaningless, because we cannot track a particle A in the crowd (cloud?) of A’s. $D_{AA}$ is not observable, so it is meaningless empirically.

If there is a spatial nonuniformity in the particle distribution, it diffuses away as described by a diffusion equation, so there is some sort of diffusion constant $D_A$. This is sometimes called the collective diffusion constant, which is observable (so meaningful). However, it is questionable that $D_A$ is related to the formula $D_{AA}$.

2 [Random walker with wind]
On a triangular lattice or a square lattice (see Fig. A & B) with the edge length $a$ is a random walker.

![Figure DH4.1: 2D random lattice walks: Triangular lattice (A) and square lattice (B)](image)

The walker starts from the origin $O$ and walks along the edges. At every second she chooses randomly any of the edges connected to her current position and moves to the nearest neighbor lattice point along the chosen edge. You can assume that she completely forgets what lattice point she was less than 1 second (i.e., all the steps are statistically independent).

(0)* After $N$ (∈ $\mathbb{N}^+$, positive integers) steps, on the average which random walker can go farther away from the origin in Fig. DH4.1 A or B? Justify your guess.

(1) What is the mean square displacement $\langle R^2 \rangle$ of the walker after $t$ seconds on the triangular lattice, where $R = (X, Y)$ is the location of the walker at time $t$?

(2) What is the mean square displacement $\langle R^2 \rangle$ of the walker after $t$ seconds on the square lattice?

(3) Now, on the square lattice due to a strong wind blowing constantly in the $+x$ direction, the walker tends to choose $+x$ direction with probability 0.5, but still chooses the remaining three directions randomly (with probability 1/6 for each).

(i) What is the average position ($x$ and $y$ coordinates) of the walker after $t$ seconds?

(ii) What is the variance of the $y$-coordinate (i.e., $V(Y)$) after $t$ seconds?

(iii)* What is the mean square displacement $\langle R^2 \rangle$ of the walker after $t$ seconds?

(iv)* Find the variance $V(X) + V(Y)$. Can this decrease due to the wind?

Soln.
(0) The same. Really? Isn’t the random walk trajectory on the triangular lattice more folded than that on the square lattice? Explain (qualitatively).

(1), (2) Let $r_i$ be the vector denoting the $i$th step. The total displacement after $t$ steps $R$
reads

\[ R = \sum_{i=1}^{t} r_i. \]  

(DH4.11)

Therefore, thanks to the statistical independence of steps and the average step displacement being zero, we obtain

\[ \langle R^2 \rangle = \sum_{i=1}^{t} \langle r_i^2 \rangle. \]  

(DH4.12)

Obviously, \( \langle r_i^2 \rangle = a^2 \), so \( \langle R^2 \rangle = ta^2 \).

* Does this calculation depend on spatial dimensionality or the lattice structure?

(3)

(i) The position after \( t \) seconds is

\[ R = \sum_{i=1}^{t} r_i. \]  

(DH4.13)

Therefore, the average position is \( \langle R \rangle = t \langle r_1 \rangle \).

\[ \langle r_1 \rangle = 0.5(a, 0) + [(-a, 0) + (0, a) + (0, -a)]/6 = (a/3, 0). \]  

(DH4.14)

Therefore, \( \langle R \rangle = ((1/3)at, 0) \).

(ii) \( Y = \sum_{i=1}^{t} y_i \), where \( y_i \) is the \( y \)-component of the \( i \)th step vector. We know \( \langle Y \rangle = 0 \), so using the statistical independence of steps, we have

\[ V(Y) = \langle Y^2 \rangle = \sum_{i=1}^{t} \langle y_i^2 \rangle, \]  

where

\[ \langle y_i^2 \rangle = (2/3) \times 0 + (1/3)a^2 = a^2/3. \]  

(DH4.15)

Therefore, \( V(Y) = a^2t/3 \).

(iii) We need

\[ \langle R^2 \rangle = \sum_{i=1}^{t} \langle r_i^2 \rangle + \sum_{i \neq j} \langle r_i \cdot r_j \rangle. \]  

(DH4.16)

Although each step is statistically independent (so you may write \( \langle r_i \cdot r_j \rangle = \langle r_i \rangle \cdot \langle r_j \rangle \)), its average is not zero in this case, so you cannot ignore the cross terms. There are \( t(t - 1) \) cross terms, but they are all the same:

\[ \langle r_i \cdot r_j \rangle = \langle r_i \rangle \cdot \langle r_j \rangle = \langle r_1 \rangle^2. \]  

(DH4.17)

We have already computed \( \langle r_1 \rangle = a/3 \). Obviously, \( \langle r_i^2 \rangle = a^2 \). Therefore, (DH4.17) reads

\[ \langle R^2 \rangle = a^2t + \frac{1}{9}a^2t(t - 1) = \frac{1}{9}a^2t^2 + \frac{8}{9}a^2t. \]  

(DH4.18)
(iv) The sum of the variances are

\[ V(X) + V(Y) = \langle R^2 \rangle - \langle X \rangle^2 - \langle Y \rangle^2 = \frac{1}{9} a^2 t^2 + \frac{8}{9} a^2 t - \left( \frac{1}{3} at \right)^2 = \frac{8}{9} a^2 t, \]  

(DH4.20)

which is smaller than \( a^2 t \).²

3 [Solving Langevin equation].
We wish to consider a Brownian particle suspended in an equilibrium fluid of temperature \( T \). Let us start with the original³ Langevin equation in the following form (but in the one dimensional space)

\[ m \frac{dv}{dt} = -\zeta v + w(t), \]  

(DH4.21)

where \( v \) is the 1D-velocity, \( m \) is the mass of the Brownian particle, \( \zeta \) is the friction constant, and \( w(t) \) is the noise force due to bombardments by molecules of the fluid.

(1) Assuming that the noise \( w(t) \) is given as a function of \( t \), find \( v \) as a function of time. You may assume that the initial velocity is \( v_0 \).

(2) If we wait for a sufficiently long time (that is, \( t \) is sufficiently large), the initial velocity should be totally forgotten, so in order to understand the long-time behavior we may assume \( v_0 = 0 \) without any loss of generality. After confirming this (or giving your argument for this), compute the ensemble average \( \langle v(t)^2 \rangle \) of \( v(t)^2 \) in terms of the time correlation function of the noise \( \varphi(s - s') = \langle w(s)w(s') \rangle \), where \( \langle \rangle \) denotes the ensemble average. Notice that since the fluid in which the particle is suspended is in equilibrium, \( \varphi \) does not depend on the absolute time, but only on the time lapse between \( s \) and \( s' \).

(3) We may assume that the noise changes so randomly and so rapidly that \( w(s) \) and \( w(s') \) at different times are statistically independent and their averages are zero. Therefore, we may write

\[ \varphi(s - s') = \langle w(s)w(s') \rangle = C \delta(s - s'), \]  

(DH4.22)

where \( C \) is a positive constant (the square noise amplitude). After a long time (i.e., in the \( t \to \infty \) limit) \( v(t) \) must be compatible with the equipartition of translational kinetic energy: \( \langle v^2(t) \rangle = k_B T/m \), so we cannot choose \( C \) arbitrarily. Find \( C \) in terms of \( k_B T \) and \( \zeta \).⁴

Soln.
(1) Solving the ODE

\[ \frac{dv}{dt} = -\left( \zeta/m \right)v + w(t)/m, \]  

(DH4.23)

²Of course, this is due to the artificial setting that the wind speed is really constant; in reality probably the wind speed fluctuates wildly, so the variance could be much larger with the wind.

³not the overdamped version.

⁴This is also a fluctuation-dissipation relation. You might wonder why the answer is different from the fluctuation-dissipation relation we discussed in the lecture. Note the difference in the definitions of the noise for overdamped and not overdamped cases.
we get (see below, if you need an explanation)

\[ v(t) = v_0 e^{-\zeta/m} t + \int_0^t ds \frac{(w(s)/m)}{e^{\zeta/m}} (t-s). \]  \hspace{1cm} (DH4.24)

**How to solve (DH4.21)**

A standard way to get this is the variation of parameters: If \( w \equiv 0 \), we easily get the general solution as

\[ v(t) = A e^{-\zeta/m} t. \]  \hspace{1cm} (DH4.25)

Now, we assume the integration constant \( A \) is a function of \( t \) as

\[ v(t) = A(t) e^{-\zeta/m} t \]  \hspace{1cm} (DH4.26)

and put this in the original ODE. We obtain

\[ A'(t) e^{-\zeta/m} t - \zeta/m A e^{-\zeta/m} t = -(\zeta/m) A e^{-\zeta/m} t + w(t)/m \]  \hspace{1cm} (DH4.27)

or

\[ A'(t) = (w(t)/m) e^{\zeta/m} t. \]  \hspace{1cm} (DH4.28)

This may be solved easily as

\[ A(t) = A(0) + \int_0^t ds \frac{(w(s)/m)}{e^{\zeta/m}}. \]  \hspace{1cm} (DH4.29)

Therefore, the general solution to the original ODE reads

\[ v(t) = A(0) e^{-\zeta/m} t + \int_0^t ds \frac{(w(s)/m)}{e^{\zeta/m} (t-s)}. \]  \hspace{1cm} (DH4.30)

We immediately identify \( A(0) = v_0 \).

(2) If \( t \) is sufficiently long, since \( m \) and \( \zeta \) are positive, the first term in our solution becomes indefinitely small, so we need not pay attention to the initial condition. We may set \( v_0 = 0 \):

\[ v(t) = \int_0^t ds \frac{(w(s)/m)}{e^{\zeta/m} (t-s)}. \]  \hspace{1cm} (DH4.31)

From this we obtain

\[ v(t)^2 = \int_0^t ds \int_0^t ds' \frac{(w(s)/m)}{e^{\zeta/m} (t-s)} \frac{(w(s')/m)}{e^{\zeta/m} (t-s')}. \]  \hspace{1cm} (DH4.32)

which, upon ensemble averaging, gives

\[ \langle v(t)^2 \rangle = \frac{1}{m^2} \int_0^t ds \int_0^t ds' e^{-(\zeta/m)(2t-s-s')} \langle w(s)w(s') \rangle = \frac{1}{m^2} \int_0^t ds \int_0^t ds' e^{-(\zeta/m)(2t-s-s')}. \]  \hspace{1cm} (DH4.33)

(3) Introducing (DH4.22) into the above equation, we get

\[ \langle v(t)^2 \rangle = \frac{C}{m^2} \int_0^t ds \int_0^t ds' e^{-(\zeta/m)(2t-s-s')} \delta(s-s'). \]  \hspace{1cm} (DH4.34)
An easy integration gives
\[
\langle v(t)^2 \rangle = \frac{C}{m^2} \int_{0}^{t} ds e^{-2(\zeta/m)(t-s)} = \frac{C}{2m\zeta} \left( 1 - e^{-2\zeta t/m} \right). \tag{DH4.35}
\]
That is, in the \( t \to \infty \) limit, we get
\[
\langle v(t)^2 \rangle \to \frac{k_B T}{m} = \frac{C}{2m\zeta}. \tag{DH4.36}
\]
Thus, we have fixed \( C \) as
\[
C = 2k_B T \zeta. \tag{DH4.37}
\]
As noted in the footnote 4, this relates the noise (amplitude squared \( C \) and the dissipation \( \zeta \)), so it is a respectable fluctuation-dissipation relation. The noise \( \nu \) in the text (the overdamped version) is \( \nu = w/\zeta \), so the amplitude of \( \nu \) is our \( C \) obtained here divided by \( \zeta^2 \). Thus, our whole story is consistent.

4 [Following Perrin using the Boltzmann factor]
Perrin counted the number of suspended Brownian particles with radius \( r = 0.212 \mu m \) with density 1206 kg/m\(^3\). His result at \( T = 288 \) K is shown in Fig. DH4.2. Since the gas constant \( R = 8.314 \) J/mol-K is obtainable from the ideal gas law (you need \( P, V \) and \( T \), and the definition of mole), from his data we can estimate Avogadro’s constant \( N_A \). How good is it?

![Figure DH4.2: Sedimentation equilibrium observed by Perrin](image)

In the figure the unit of the concentration may be anything, since we need only the ratios.

**Soln.**
This is a simple Boltzmann factor question. The potential energy difference of the particle of radius \( r \) due to the height difference \( h \) is, if the particle of density \( \rho \) is suspended in a fluid of density \( \rho_0 \), \((4\pi r^3/3)(\rho - \rho_0)gh\); you must take the buoyancy into account. Therefore, the number density \( n(h) \) at height \( h \) obeys
\[
n(h) = n(0) \exp \left( \frac{-(4\pi r^3/3)(\rho - \rho_0)ghN_A}{RT} \right), \tag{DH4.38}
\]
where $R$ is measurable using an ideal gas. The experimental result can give $a$:

$$\log \frac{n(h)}{n(0)} = -\frac{(4\pi r^3/3)(\rho - \rho_0)ghN_A}{RT} = -ah$$  \hspace{1cm} (DH4.39)

Therefore, we can calculate

$$a = \frac{(4\pi r^3/3)(\rho - \rho_0)gN_A}{RT} = \frac{(4\pi(0.212 \times 10^{-6})^3/3)(1206 - 1000) \times 9.8N_A}{8.314 \times 288} = 0.0337 \times 10^{-18} N_A.$$  \hspace{1cm} (DH4.40)

The slope is obtained from the graph Fig. DH4.2; roughly,

$$a = \left(\log \frac{100}{12}\right)/95 \times 10^{-6} = 2.23 \times 10^4.$$  \hspace{1cm} (DH4.41)

Thus, $N_A = (2.23 \times 10^4/3.37 \times 10^{-20}) = 6.6 \times 10^{23}$. Perhaps, too good.