Lecture 4

Differential equation formulation

Recall that

$$W(\vec{R}) = \left(\sqrt{\frac{3}{2\pi n\langle r^2\rangle t}}\right)^3 e^{-\frac{3|\vec{R}|^2}{2n\langle r^2\rangle t}}$$

Define $D = \frac{n\langle r^2\rangle}{6}$, then

$$W(\vec{R}) = \frac{1}{(4\pi D t)^{3/2}} e^{-\frac{|\vec{R}|^2}{4Dt}} \qquad (1)$$

Can we obtain this as a solution of some differential eq'n?

Think of an ensemble of particles rather than a single particle : prob. → fraction of particles

Consider Δt s.t. a particle suffers many displacements ("makes many steps") but

$$\underbrace{\sqrt{\langle|\Delta\vec{R}|^2\rangle}}_{\text{rms displacement}} \ll \vec{R} \qquad (*)$$

indep. of $\vec{R}$

Then $\Psi(\Delta R;\Delta t) = \frac{1}{(4\pi D\Delta t)^{3/2}} e^{-\frac{|\Delta\vec{R}|^2}{4D\Delta t}}$

prob. density that a particle suffers a net displacement $\Delta\vec{R}$ in time Δt

Consequently, $W(\vec{R}, t+\Delta t) = \int_{-\infty}^{\infty} d(\Delta\vec{R})\, \underbrace{W(\vec{R}-\Delta\vec{R}, t)}_{\text{can expand due to } (*)}\, \Psi(\Delta\vec{R};\Delta t)$

Then

$$W(\vec{R}, t+\Delta t) = \frac{1}{(4\pi D \Delta t)^{3/2}} \int_{-\infty}^{\infty} d(\Delta X)\, d(\Delta Y)\, d(\Delta Z) \times$$

$$\times\, e^{-\frac{|\Delta \vec{R}|^2}{4 D \Delta t}} \Big\{ W(\vec{R}, t) - \Delta X \frac{\partial W}{\partial X} - \Delta Y \frac{\partial W}{\partial Y} - \Delta Z \frac{\partial W}{\partial Z} +$$

$$+ \frac{1}{2}\Big[(\Delta X)^2 \frac{\partial^2 W}{\partial X^2} + (\Delta Y)^2 \frac{\partial^2 W}{\partial Y^2} + (\Delta Z)^2 \frac{\partial^2 W}{\partial Z^2} +$$

$$+ 2\Delta X \Delta Y \frac{\partial^2 W}{\partial X \partial Y} + 2 \Delta Y \Delta Z \frac{\partial^2 W}{\partial Y \partial Z} + 2 \Delta Z \Delta X \frac{\partial^2 W}{\partial Z \partial X}\Big] +$$

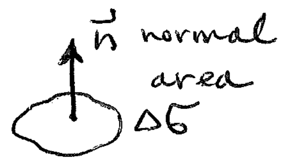
$$+ \dots \Big\} = W(\vec{R}, t) + D \Delta t \left(\frac{\partial^2 W}{\partial X^2} + \frac{\partial^2 W}{\partial Y^2} + \frac{\partial^2 W}{\partial Z^2} \right) + O(\Delta t^2).$$

$$\langle \Delta X \rangle = \langle \Delta Y \rangle = \langle \Delta Z \rangle = 0$$

$$\langle \Delta X \Delta Y \rangle = \langle \Delta X \rangle \langle \Delta Y \rangle = 0, \text{ etc.}$$

So, $\dfrac{\partial W}{\partial t} = D\left(\dfrac{\partial^2 W}{\partial X^2} + \dfrac{\partial^2 W}{\partial Y^2} + \dfrac{\partial^2 W}{\partial Z^2} \right)$ is the DE for which (1) is the solution.

Consider



\# particles crossing $\Delta\sigma$ in time Δt is:

$$\underbrace{-D(\vec{n} \cdot \vec{\nabla} W)}_{\text{diffusion current density projected onto } \vec{n} \,:\, \vec{n}\cdot\vec{J}} \Delta\sigma\, \Delta t$$

Note that $\dfrac{\partial W}{\partial t} + (-D)\vec{\nabla}^2 W = 0$, or

$$\frac{\partial W}{\partial t} + \vec{\nabla} \cdot \underset{\substack{\parallel \\ -D\vec{\nabla} W}}{\vec{J}} = 0 \quad \text{continuity eq'n}$$

$-D\vec{\nabla}W$ diffusion current density

BCs: (i) $W=0$ on every element of a perfectly absorbing surface

(ii) $\{\vec{n}\cdot\vec{\nabla}W\}=0$ on every element of a perfectly reflecting surface

Current density into the absorbing surface: $-D(\vec{n}\cdot\vec{\nabla}W)\Big|_{W=0}$

$\uparrow$ normal to the absorbing surface

In general, 1st moments do not disappear:
[$\tau(\vec{r})$ is not symmetric:] $\tau(\vec{r})=\tau(|\vec{r}|)$ anymore

$$W(\vec{R})=\frac{1}{\sqrt{(2\pi N)^3\langle x^2\rangle\langle y^2\rangle\langle z^2\rangle}}\times$$

$$\times\, e^{-\frac{(X-N\langle x\rangle)^2}{2N\langle x^2\rangle}-\frac{(Y-N\langle y\rangle)^2}{2N\langle y^2\rangle}-\frac{(Z-N\langle z\rangle)^2}{2N\langle z^2\rangle}}$$

Define
$$\begin{cases} D_1=\frac{n\langle x^2\rangle}{2}, \quad D_2=\frac{n\langle y^2\rangle}{2}, \quad D_3=\frac{n\langle z^2\rangle}{2} \\ \beta_1=-n\langle x\rangle, \quad \beta_2=-n\langle y\rangle, \quad \beta_3=-n\langle z\rangle \end{cases}$$
"velocities"

Then
$$W(\vec{R})=\frac{1}{8(\pi t)^{3/2}\sqrt{D_1D_2D_3}}\times$$

$$\times\, e^{-\frac{(X+\beta_1 t)^2}{4D_1 t}-\frac{(Y+\beta_2 t)^2}{4D_2 t}-\frac{(Z+\beta_3 t)^2}{4D_3 t}}$$

As before, consider

$$\Psi(\Delta\vec{R};\Delta t) = \frac{1}{8(\pi\Delta t)^{3/2}\sqrt{D_1D_2D_3}} \times$$

$$\times\, e^{-\frac{(\Delta X+\beta_1\Delta t)^2}{4D_1\Delta t} - \frac{(\Delta Y+\beta_2\Delta t)^2}{4D_2\Delta t} - \frac{(\Delta Z+\beta_3\Delta t)^2}{4D_3\Delta t}}.$$

Then

$$W(\vec{R},t+\Delta t) = \int_{-\infty}^{\infty} d(\Delta\vec{R})\, W(\vec{R}-\Delta\vec{R},t)\Psi(\Delta\vec{R};\Delta t) =$$

$$= \frac{1}{8(\pi\Delta t)^{3/2}\sqrt{D_1D_2D_3}} \int_{-\infty}^{\infty} d(\Delta X)d(\Delta Y)d(\Delta Z)\,\times$$

$$\times \Big\{ W(\vec{R},t) - \left(\Delta X\frac{\partial W}{\partial X} + \Delta Y\frac{\partial W}{\partial Y} + \Delta Z\frac{\partial W}{\partial Z}\right) +$$

$$+\frac{1}{2}\Big(\Delta X^2\frac{\partial^2 W}{\partial X^2} + \Delta Y^2\frac{\partial^2 W}{\partial Y^2} + \Delta Z^2\frac{\partial^2 W}{\partial Z^2} +$$

$$+\ 2\Delta X\Delta Y\frac{\partial^2 W}{\partial X\partial Y} + 2\Delta Y\Delta Z\frac{\partial^2 W}{\partial Y\partial Z} +$$

$$+2\Delta Z\Delta X\frac{\partial^2 W}{\partial Z\partial X}\Big) + \dots \Big\}\, e^{-\frac{(\Delta X+\beta_1\Delta t)^2}{4D_1\Delta t}} \times$$

$$\times\, e^{-\frac{(\Delta Y+\beta_2\Delta t)^2}{4D_2\Delta t}}\, e^{-\frac{(\Delta Z+\beta_2\Delta t)^2}{4D_3\Delta t}}.$$

Clearly,
$$\begin{cases} \langle\Delta X\rangle = -\beta_1\Delta t \\ \langle\Delta Y\rangle = -\beta_2\Delta t \\ \langle\Delta Z\rangle = -\beta_3\Delta t \end{cases} \qquad \theta(\Delta t)$$

$$\langle\Delta X^2\rangle = 2D_1\Delta t + \underbrace{\beta_1^2\Delta t^2}_{\theta(\Delta t^2)} \quad ,\text{etc.}$$

$$\langle \Delta X \Delta Y \rangle = \langle \Delta X \rangle \langle \Delta Y \rangle = \beta_1 \beta_2 \Delta t^2 \leftarrow O(\Delta t^2),$$
etc.

So,

$$\frac{\partial W}{\partial t} = D_1 \frac{\partial^2 W}{\partial X^2} + D_2 \frac{\partial^2 W}{\partial Y^2} + D_3 \frac{\partial^2 W}{\partial Z^2} + $$
$$+ \beta_1 \frac{\partial W}{\partial X} + \beta_2 \frac{\partial W}{\partial Y} + \beta_3 \frac{\partial W}{\partial Z} .$$

$$\frac{\partial W}{\partial t} = \underset{\substack{\| \\ D_i \delta_{ij}}}{D_{ij}} \frac{\partial^2 W}{\partial X_i \partial X_j} + \beta_i \frac{\partial W}{\partial X_i} . \qquad (2)$$

in more modern notation

Can define diffusion currents again, e.g. current density $\perp$ X axis is given by:

$$\underbrace{-\beta_1 W}_{\text{drift}} - \underbrace{D_1 \frac{\partial W}{\partial X}}_{\text{diffusion}} \quad , etc.$$

Eq'n (2) is solved by:

$$W = \frac{\overset{\swarrow \text{normal'n const}}{C}}{\sqrt{D_1 D_2 D_3 t^3}} \, e^{-\frac{(X-X_0+\beta_1 t)^2}{4D_1 t} - \frac{(Y-Y_0+\beta_2 t)^2}{4D_2 t} - \frac{(Z-Z_0+\beta_3 t)^2}{4D_3 t}}$$

, just as above

The theory of the Brownian motion

Liquid @ room T : a Brownian particle undergoes $\sim 10^{21}$ collisions/sec, too many to treat explicitly. Instead, use Langevin's equation; for a <u>free</u> particle it's given by:

$\vec{u}$ - part. velocity

$$\frac{d\vec{u}}{dt} = \underbrace{-\beta\vec{u}}_{\text{friction}} + \underbrace{\vec{A}(t)}_{\text{fluctuations}} \qquad (*)$$

If the particle is spherical with radius a, $\beta = \frac{6\pi a \eta}{m}$

η - coeff. of viscosity
m - part. mass

Two assumptions about $\vec{A}(t)$:

(i) $\vec{A}(t)$ is indep. of $\vec{u}$
(ii) $\vec{A}(t)$ varies much faster than $\vec{u}$

(ii) means that for a Δt s.t.

$$\vec{u}(t+\Delta t) \simeq \vec{u}(t) + \frac{d\vec{u}}{dt}\Delta t ,$$

$\vec{A}(t)$ is <u>not</u> correlated with $\vec{A}(t+\Delta t)$

Define $W(\vec{u}, t; \vec{u}_0)$ = velocity prob. density

$\vec{u}$: velocity at t; $\vec{u}_0$: init. velocity at $t=0$

Clearly, $W(\vec{u},t;\vec{u}_0) \to \delta(\vec{u}-\vec{u}_0)$ as $t \to 0$

Furthermore,

$$W(\vec{u},t;\vec{u}_0) \to \underbrace{\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{m|\vec{u}|^2}{2k_BT}}}_{\text{equil. Maxwell's distr'n}} \quad \text{as } t\to\infty$$

This last condition imposes some constraints on the distr'n of $\vec{A}(t)$.

Consider the formal solution of (*):

$$\vec{u} = \vec{u}_0 e^{-\beta t} + e^{-\beta t}\int_0^t d\xi\, e^{\beta\xi}\vec{A}(\xi).$$

We see that the distr'n of $\vec{u}-\vec{u}_0 e^{-\beta t}$ [which $\to \vec{u}$ as $t\to\infty$] is the same as the distr'n for

$$e^{-\beta t}\int_0^t d\xi\, e^{\beta\xi}\vec{A}(\xi).$$

So, $\lim_{t\to\infty}\left\{e^{-\beta t}\int_0^t d\xi\, e^{\beta\xi}\vec{A}(\xi)\right\}$ should follow Maxwell's distr'n.

Now, $e^{-\beta t}\int_0^t d\xi\, e^{\beta\xi}\vec{A}(\xi) =$

$$= e^{-\beta t}\sum_j e^{\beta j\Delta t}\int_{j\Delta t}^{(j+1)\Delta t} d\xi\, \vec{A}(\xi) =$$

$$= \sum_j e^{\beta(j\Delta t - t)}\underbrace{\vec{B}(\Delta t)}_{``\int_t^{t+\Delta t} d\xi \vec{A}(\xi)\text{, indep. of } j}$$

$\vec{B}(\Delta t)$ is the change in velocity over Δt.

Finally, $\vec{u} - \vec{u}_0 e^{-\beta t} = \sum_j e^{\beta(j\Delta t - t)} \vec{B}(\Delta t)$.

Now we will assert a gaussian distribution for $\vec{B}(\Delta t)$ and show that it is consistent with $W(\vec{u}, t; \vec{u}_0) \to$ $\to$ Maxwell's distr'n as $t \to \infty$:

$$w(\vec{B}) = \frac{1}{(4\pi q \Delta t)^{3/2}} e^{-\frac{|\vec{B}(\Delta t)|^2}{4q\Delta t}}, \qquad (***)$$

$$q = \frac{\beta k_B T}{m}.$$

Indeed, it should be gaussian due to a large number of collisions over Δt.

<u>Lemma</u> Let $\vec{R} = \int_0^t d\xi\, \psi(\xi) \vec{A}(\xi)$

Divide $(0, t)$ into a large number of intervals Δt:

$$\vec{R} \simeq \sum_j \underbrace{\psi(j\Delta t)}_{\text{smooth } f'n} \overbrace{\int_{j\Delta t}^{(j+1)\Delta t} \vec{A}(\xi)\, d\xi}^{\vec{B}(\Delta t)} =$$

$$= \sum_j \underbrace{\overbrace{\psi(j\Delta t)}^{\equiv \psi_j} \vec{B}(\Delta t)}_{\equiv \vec{F}_j \text{, just like RWs}}.$$

But (***) implies that

$$\tau(\vec{r}_j) = \frac{1}{(4\pi q \Psi_j^2 \Delta t)^{3/2}} e^{-\frac{|\vec{r}_j|^2}{4q\Psi_j^2 \Delta t}} =$$

$$= \frac{1}{(2\pi \ell_j^2/3)^{3/2}} e^{-\frac{3|\vec{r}_j|^2}{2\ell_j^2}}, \quad \text{where}$$

isotropic gaussian distr'n of step lengths

$$\ell_j^2 = 6q\Psi_j^2 \Delta t.$$

From previous work on RWs:

$$W(\vec{R}) = \frac{1}{\left(2\pi \sum_j \ell_j^2/3\right)^{3/2}} e^{-\frac{3|\vec{R}|^2}{2\sum_j \ell_j^2}}, \quad \text{where}$$

$$\sum_j \ell_j^2 = 6q\sum_j \Psi^2(j\Delta t)\,\Delta t = 6q\int_0^t d\xi\, \Psi^2(\xi).$$

Finally,

$$W(\vec{R}) = \frac{1}{\left[4\pi q \int_0^t d\xi\, \Psi^2(\xi)\right]^{3/2}} e^{-\frac{|\vec{R}|^2}{4q\int_0^t d\xi \Psi^2(\xi)}}.$$

In our case, $\Psi(\xi) = e^{\beta(\xi - t)}$ and

$$\int_0^t d\xi\, \Psi^2(\xi) = \frac{1 - e^{-2\beta t}}{2\beta}.$$

$\frac{q}{\beta} = \frac{k_B T}{m}$

Then $W(\vec{u} - \vec{u}_0 e^{-\beta t}, t; \vec{u}_0) =$

$$\overset{\textcircled{=}}{} \left[\frac{m}{2\pi k_B T(1-e^{-2\beta t})}\right]^{3/2} e^{-\frac{m|\vec{u}-\vec{u}_0 e^{-\beta t}|^2}{2k_B T(1-e^{-2\beta t})}} .$$

As $t \to \infty$, we obtain:

$$W(\vec{u}, t; \vec{u}_0) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{m|\vec{u}|^2}{2k_B T}} .$$

Maxwell's distr'n