Thermal Physics

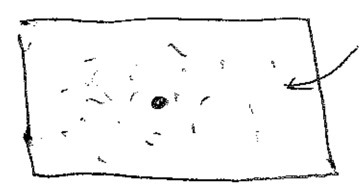
Dec 3rd, 2014

I Brownian Motion and the Langevin Equation

II Measuring k_B

I A macroscopic but small particle immersed in a fluid will move about randomly – this is called Brownian motion.

This is an equilibrium phenomenon but the motion is due to the fluctuations about the equilibrium value and so it is a nice gateway into nonequilibrium thinking. It is also closely tied to the process of dissipation of energy.



1D Brownian motion particle of mass m with com position $x(t)$ and velocity

$$v = \frac{dx}{dt}$$

Describe the interaction with the fluid as an effective force $F(t)$.

Any external forces (e.g. gravity) are $\mathcal{F}(t)$

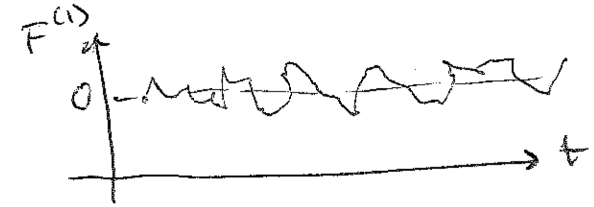
We have

don't know much about this

$$m \frac{dv}{dt} = \mathcal{F}(t) + F(t)$$

So, consider an ensemble of systems and treat F as a random function of t — try to treat the problem in a statistical manner. For example

System 1



System 2

etc.

Characterize F as follows:

- "correlation time" τ^* measures mean time between successive maxima (roughly $\frac{\ell}{v} \sim 10^{-13}$ sec)

- No preferred direction $\overline{F(t)} = 0$

What statistical statements can we make about v? Certainly it is fluctuating, so write

$$v = \underbrace{\bar{v}}_{\text{slow variation}} + \underbrace{v'}_{\text{rapidly fluctuating}}$$

$\bar{v}$ is important for long time behavior. We calculate

$$\int_t^{t+\tau} m \frac{dv}{dt} = \int_t^{t+\tau} \left[\mathcal{F}(t) + F(t)\right] dt$$

with $\tau \gg \tau^*$

assumed to vary slower than τ scale

$$\Rightarrow m\left[v(t+\tau) - v(t)\right] = \mathcal{F}(t)\,\tau + \int_t^{t+\tau} F(t)\,dt$$

To get at the interesting physics we should also decompose F,

$$F = \overline{F} + \underbrace{F'}_{\text{average } = 0}$$

If $\bar{v}=0$ then we should have $\bar{F}(\bar{v})=0$. This means that for small $\bar{v}$ we can Taylor expand

$\bar{F}$ tends to decrease v

$$\bar{F} = 0 - \alpha\bar{v} + \cdots$$

positive "friction constant"

Putting this all together we get

$$m\frac{dv}{dt} = \mathcal{F} - \alpha\bar{v} + F'(t)$$

or

$$\boxed{m\frac{dv}{dt} \simeq \mathcal{F} - \alpha v + F'(t)}$$

purely random and such that $\bar{F}'=0$.

This dissipation connects to a big question: If $A+B$ has reversible dynamics; when is it possible to describe B approximately by irreversible dynamics? what are effective equations for A?

environment, here a liquid

system, here a particle

II Let's turn to finding a consequence of the Langevin equation — the mean square displacement

where the last follows from $\alpha\bar{v} \simeq \alpha v$

Since v' should be small compared to F' due to the macroscopic mass m.

The last is the Langevin equation.

Before turning to consequences of this equation note the presence of friction $-\alpha v$

$$\overline{x^2} \equiv \langle x^2 \rangle$$

new notation for ensemble average

For $\mathcal{F}=0$ we have

$$m\frac{d\dot{x}}{dt} = -\alpha\dot{x} + F'(t)$$

with α given by Stoke's law

$$\alpha = 6\pi\eta a$$

radius of spherical particle

fluid viscosity.

Things get simpler if we multiply by x to get

$$m\, x \frac{d\dot{x}}{dt} = -\alpha\, x\dot{x} + x F'$$

Note that

$$x \frac{d\dot{x}}{dt} = \frac{d}{dt}(x\dot{x}) - \dot{x}^2$$

So

$$m \frac{d}{dt}(x\dot{x}) = m\dot{x}^2 - \alpha\, x\dot{x} + x F'$$

Take average $\langle\ \rangle$ to find

$$m\left\langle \frac{d}{dt}(x\dot{x})\right\rangle = m\langle \dot{x}^2\rangle - \alpha\langle x\dot{x}\rangle + \langle x F'\rangle$$

But $\langle \tfrac{1}{2} m\dot{x}^2\rangle = \tfrac{1}{2}kT$ and

$$\langle x F'\rangle = \langle x\rangle\langle F'\rangle = 0$$

independent variables

So

$$m \frac{d}{dt}\langle x\dot{x}\rangle = kT - \alpha\langle x\dot{x}\rangle$$

This we can solve

$$\langle x\dot{x}\rangle = C e^{-\gamma t} + \frac{kT}{\alpha}$$

with

$$\gamma = \frac{\alpha}{m}$$

The initial condition $x(0)=0$ gives

$$C = -\frac{kT}{\alpha}$$

so that

$$\langle x\dot{x}\rangle = \frac{kT}{\alpha}\left(1 - e^{-\gamma t}\right)$$

But

$$\langle x\dot{x}\rangle = \frac{1}{2}\frac{d}{dt}\langle x^2\rangle$$

So

$$\frac{d\langle x^2\rangle}{dt} = \frac{2kT}{\alpha}\left(1 - e^{-\gamma t}\right)$$

and

$$\langle x^2\rangle = \frac{2kT}{\alpha}\left[t - \gamma^{-1}\left(1 - e^{-\gamma t}\right)\right]$$

<u>Limits</u>: If $t \ll \gamma^{-1}$ then

$$1 - e^{-\gamma t} = 1 - \left(1 - \gamma t + \tfrac{1}{2}\gamma^2 t^2 + \dots\right)$$

and

$$\langle x^2 \rangle \simeq \frac{kT}{m} t^2 \quad \text{or} \quad \sqrt{\langle x^2 \rangle} = \sqrt{\frac{kT}{m}}\, t$$

So the ~~particles~~ particle behaves like a free particle with velocity

$$v = \sqrt{\frac{kT}{m}}$$

for short times. For longer times $t \gg \gamma^{-1}$

$$\langle x^2 \rangle = \frac{2kT}{\gamma} t$$

Doing this in Paul's lab will be one of your homework problems for next week.

We're back where we started the course — it behaves like a random walk! Explicitly

$$\langle x^2 \rangle = 2 \underbrace{\left(\frac{kT}{6\pi\eta a}\right)}_{\text{called the "diffusion coefficient"}} t$$

If you know T, a and η you can measure k! Very cool.