Thermal Physics

Dec. 8th, 2014

I Last ~~time~~ time

II What is nonequilibrium?

III Markov processes

I • Langevin equation

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

purely random and s.t. $\overline{F'} = 0$

• Derived Brownian motion as a consequence of this equation

For times $t \gg \gamma^{-1}$

$$\langle x^2 \rangle = 2Dt$$

with "diffusion coefficient"

$$D = \frac{kT}{6\pi\eta a}$$

II Our equilibrium considerations have led us to focus on

$$P_r = e^{-\beta E_r}/Z$$

r labels state ~~or~~ classical "configuration"

Because of the equilibrium assumption this distribution didn't change in time — but away from equilibrium it certainly will. So we turn to a study of

$$P_r(t).$$

In other words, a facet of

nonequilibrium is the study of evolving probability distributions.

We could continue to attack this along similar lines to our study of Brownian motion and the Langevin eqn. — this would be the "continuum" approach and leads to the "Fokker-Planck" equation.

However, I find the discrete approach slightly more intuitive and in the end it turns out to be mathematically more developed and general. So let's discretize.

III First discretize time into steps of length δt,

$$\tau = 0, 1, \ldots \text{ of time } \delta t$$

Label states (or configurations) by r,

$$C_1, C_2, \ldots, C_r, \ldots$$

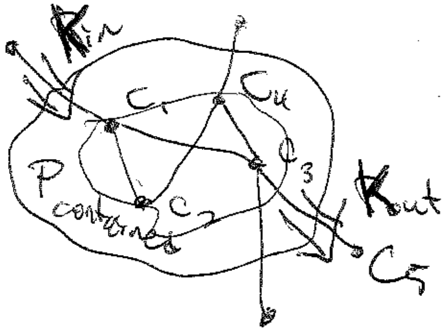
Define

$$P_r(\tau) \equiv P(C_r, \tau\,\delta t)$$

Because the total probability is conserved

$$\sum_r P_r(\tau) = 1$$

the probability P must satisfy a continuity equation. That is the change in probability ~~density~~ in time should be due to "probability" currents



Denote the currents by

$$K^s_r(\tau) \equiv K(C_s \to C_r, \tau\delta t)$$

The net current satisfies

$$K^r_s(\tau) = - K^s_r(\tau)$$

and its divergence is

$$\sum_s K^s_r(\tau)$$

In general K is a new variable and we need to find an equation for how it evolves.

We introduce a <u>simplifying</u> <u>assumption</u> $K^s_r \propto P_s$

This leads to a "Markov chain" or "Master equation" and implies a very specific claim about the evolution — the future evolution only depends on the present state.

We write

$$P_r(\tau+1) = \sum_s \omega^s_r P_r(\tau)$$

where

ω^s_r = transition rate from C_s to C_r.

We'll take the ω^s_r as given structure in the problem description.

Probability conservation imposes

$$\sum_r \omega^s_r = 1$$

We summarise all of this in the equation

$$\Delta P_r(\tau) \equiv P_r(\tau+1) - P_r(\tau)$$

$$= \sum_{s \neq r} \left[\omega^s_r P_s(\tau) - \omega^r_s P_r(\tau) \right]$$

We can view this as a Matrix eqn.

$$\Delta P_r(\tau) = \sum_s L^s_r P_r(\tau)$$

with

$$L^s_r = \begin{cases} \omega^s_r & r \neq s \\ -\sum_{k \neq s} \omega^s_k & r = s \end{cases}$$

$$\frac{dP_r}{dt} = P_{r+1} + P_{r-1} - 2P_r$$

$$L = \begin{pmatrix} \ddots & & & & & & \\ 0 & 1/2 & -1 & 1/2 & 0 & & \\ 0 & 0 & 1/2 & -1 & 1/2 & 0 & \\ 0 & 0 & 0 & 1/2 & -1 & 1/2 & \\ & & & & & & \ddots \end{pmatrix}$$

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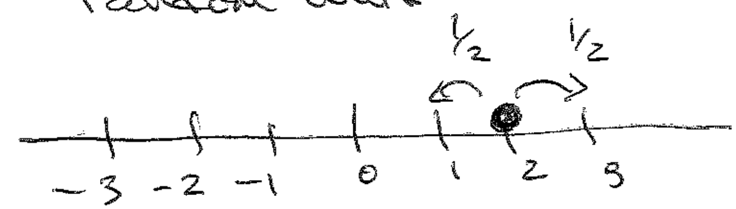
Simple Example: Discrete random walk



$$L = \begin{pmatrix} \ddots & & & & & & \\ 0 & 1 & -2 & 1 & 0 & & \\ 0 & 0 & 1 & -2 & 1 & 0 & \\ 0 & 0 & 0 & 1 & -2 & 1 & \\ & & & & & & \ddots \end{pmatrix}$$