Stat Phys! <u>averages</u> FK7029

(21)

<u>Boltzmann:</u> reversible microscopic $\longleftrightarrow$ irreversible decay to equilibrium
<u>statistical assumptions</u>, coarse graining, Stoßzahlansatz

<u>Ergodicity</u> where does it go after long time?

particles don't know about eachother

coarse graining
some sort of distribution
$\mu(\gamma)$ <u>ergodic measure</u>

- ⇒ If it exists, it's unique

$$\langle A \rangle_{time} = \langle A \rangle_{\mu(\gamma)}$$ time average = ensemble average.

- hard to prove, ergodic/chaotic hypothesis

theoretical — equilibrium exists
— $\mu(\gamma)$ tells us what it looks like (not everything)
⇒ Equilibrium Stat Phys.

computational : — allows for reduction of system (MC)
— can induce various ensembles to represent physical situations
— helps with calculation of averages

<u>Watch out:</u> not all systems are really ergodic on your time scales classes

~~INSERT AVERAGING HERE~~

Constant parameters

- $\underbrace{N\ V\ E}$ T P μ

└ what we have been doing so far, microcanonical

- $\mu(\gamma)$ says : all states equally likely.
equal amounts of time in equal amounts of phase space

Ω # states with energy E, or volume of energy shell

entropy $S = k_B \log \Omega$

macroscopic quantities go to most common values, i.e max S

⇒ second law of thermodynamics.

$$T = \left(\frac{\partial S}{\partial E}\right)^{-1}_{N,V} \qquad \mu = -T\left(\frac{\partial S}{\partial N}\right)_{E,V} \qquad P = T\left(\frac{\partial S}{\partial V}\right)_{E,N}$$

1st law: $dE = T\,dS - P\,dV + \mu\,dN$.

Determination of error in averages etc. also to do with correlations

often stuff expressed as averages

i.e $C_V = \left.\frac{\partial E}{\partial T}\right|_{N,V}$

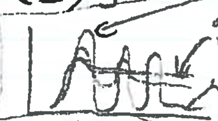
$$Z = \frac{1}{N!}\sum_i \exp(-\beta E_i)$$

$$\langle E\rangle = \frac{1}{N!Z}\sum_i E_i \exp(-\beta E_i) =$$

$$= -\beta^2 \frac{\partial}{\partial\beta}\langle E\rangle$$

$$= -\beta^2\left\{\frac{1}{N!Z}\sum_i -E_i^2 \exp(-\beta E_i) + \frac{1}{N!Z^2}\left[\sum_i E_i \exp(-\beta E_i)\right]^2\right\} = \beta^2\left[\langle E^2\rangle - \langle E\rangle^2\right]$$

similar, pressure $\langle p\rangle$ at boundary etc..
RDF is average populations etc



some things are harder (not derivatives of Z or something else obvious)
F or G, S, μ → maybe more later on in course

evaluating averages is easy. Error due to finite size

finite time
$\langle A\rangle$ is average of A, SD $\sigma = \langle A^2\rangle - \langle A\rangle^2$ ← finite time
time averages, temporal correlation, so not independ realisations.
(so not just error = $\sigma/\sqrt{\#\text{terms averaged}}$
→ should be # independent samples

estimate the correlation time via (or length)
correlation function

$$C_{AA}(k) = \langle (A_n - \langle A\rangle)(A_{n+k} - \langle A\rangle)\rangle \qquad C_{AA}(0) = \sigma^2, \text{ then falls off}$$

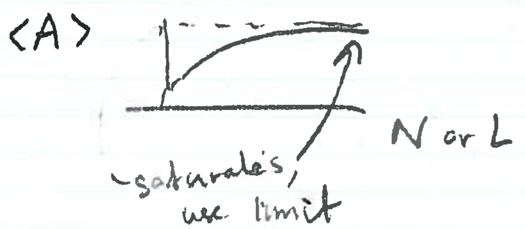
number of ways to get corr tim τ from this.

- fit to exp part,
- $\tau = \frac{1}{2}\sum_{n=-\infty} \frac{C_{AA}(n)}{C_{AA}(0)}$ (same for C_{AA} exponential in n

estimating error (see book) ⇒ $\text{error}^2 = \frac{2\tau}{\#\text{samples}}\sigma^2$

Alternatively: just devide into large blocks of length $> \tau$, calculate seperate averages for each.
Now you have small number of independent samples.

Finite size systematic error



(assuming for $N \to \infty$ not dependent on N) hard to keep E constant in experiment (heat bath)

T instead ⇒ canonical ensemble. NVT constant.
most common

$\mu(\gamma) \propto \exp(-\beta E)$ $\beta = \frac{1}{\tau} = \frac{1}{k_B T}$
Boltzman factor.

⇒ normalisation with partition function

$\langle A \rangle_{NVT} = \frac{1}{N!Z} \sum_{states} A \; e^{-\beta E(state)}$

$Z(N,V,T) = \frac{1}{N!} \sum_{states} e^{-\beta E(state)} = \sum_E e^{-\beta E} \Omega(NVE) = \sum_E e^{-\beta(E-TS)}$

$F = T \log Z = E - TS.$

minimised in equilibrium in canonical ensemble.

There are 2 more

- isothermal, isobaric NPT pressure constant
  Gibbs. $G = E - TS + pV$ $\mu(\gamma) = \exp(-\beta E - \beta pV)$
- grand canonical μVT open system $(-\beta E - \beta \mu N)$

How to achieve NVT in simulations (or part of simulated system): must couple to effective heat bath. Thermostats

- experiments / real systems have heat baths.
- sometimes you need to remove energy, because you are putting it in
- non-physical constructs: take extreme care
- examples: Langevin, Nosé-Hoover

end lecture 6

Langevin damping random force gaussian uncorrelated noise NOT DETERMINIS[TIC]

$\dot{x} = v$

$\dot{v} = -\eta v + a(t) + \xi(t)$

drift x_η $F = \eta m v = \gamma v$

assumptions: bath is fast & correlation decays exponentially
adiabatic, damping is viscous.

example: 1D system, $V(x)$

Fokker-Planck equation $p(x,v)$ probability density

$\frac{d}{dt} p(x,v) = \frac{\partial}{\partial v}[(a(x) - \eta v)\, p(x,v)] + \frac{\partial}{\partial v}\frac{\partial}{\partial v} D_{vv} \; p(x,v)$

$+ \frac{\partial}{\partial x}(v p)$

drift diffusion

$p(x,v)$

drift: $\frac{dp(v)}{dv} = dt \cdot p(v+dv)\, \dot{v}(v+dv) - \dot{v}$