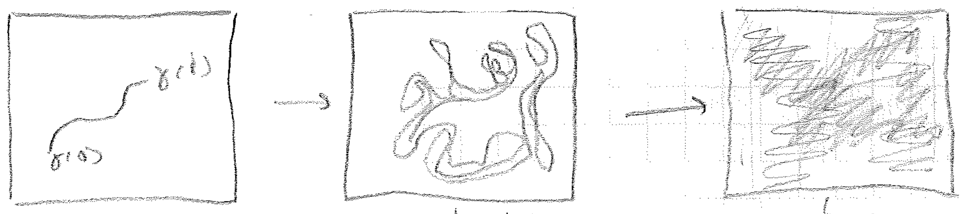
Stat Phys! averages FK7029

(19)

Boltzmann: reversible microscopic $\longleftrightarrow$ irreversible decay to equilibrium

statistical assumptions, coarse graining, Stoßzahlansatz $\to$ particles don't know about eachother

Ergodicity where does it go after long time?



$\gamma(t)$, t large

$t \to \infty$

coarse graining

Some sort of distribution

$\mu(\gamma)$ ergodic measure

$\Rightarrow$ If it exists, it's unique

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

hard to prove, ergodic/chaotic hypothesis

theoretical : - equilibrium exists

- $\mu(\gamma)$ tells us what it looks like (not everything)

$\Rightarrow$ Equilibrium Stat Phys.

computational : - allows for reduction of system (MC)

- can induce various ensembles to represent physical situations

- helps with calculation of averages

Watch out: not all systems are really ergodic on your time scales (classes)

~~INSERT AVERAGING HERE~~ (next page)

Constant parameters

$$\underbrace{N \quad V \quad E}_{} \quad T \quad P \quad \mu$$

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

$\Rightarrow$ 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

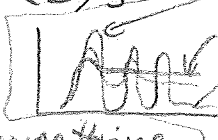
i.e. $C_V = \left.\frac{\partial E}{\partial T}\right|_{N,V}$ $\qquad Z = \frac{1}{N!}\sum_i \exp(-\beta E_i)$

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

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

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

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

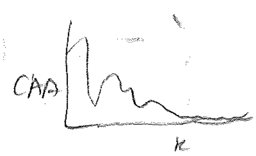
$\langle A\rangle$ is average of A, SD $\sigma = \langle A^2\rangle - \langle A\rangle^2$ ← finite time

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

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

number of ways to get corr tim τ from this.

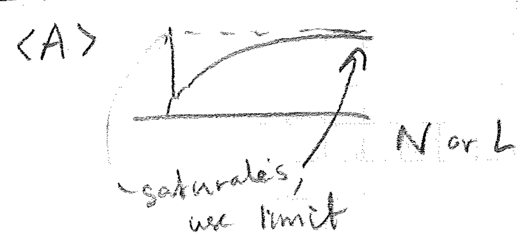


- fit exponential function
- $\tau = \frac{1}{2}\sum_{n=-\infty}^{\infty}\frac{C_{AA}(n)}{C_{AA}(0)}$ (same for C_{AA} exponential in n)

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

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

Finite size systematic error



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

T instead $\Rightarrow$ canonical ensemble. NVT constant.
most common

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

$\Rightarrow$ normalisation with partition function

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

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

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

minimised in equilibrium in canonical ensemble.

There are 2 more

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

end lecture 6

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

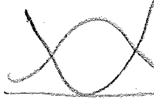
- experiments/real systems have heat baths.
- sometimes you need to remove energy, because you are putting it in
- non-physical constructs: take extreme care
- examplos: Langevin, Nosé-Hoover

Langevin damping random force gaussian uncorrelated noise NOT DETERMINISTIC

$$\dot{x} = v$$
$$\dot{v} = \underbrace{-\eta v + a(t)}_{\text{drift } a_\eta} + \xi(t)$$
$$F = \eta m v = \gamma v$$

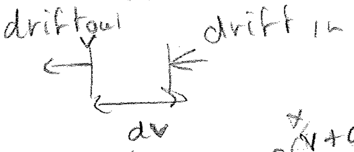
assumptions: bath is fast & correlation decays exponentially adiabatic, damping is viscous.

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



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

$$\frac{d}{dt}p(x,v) = \underbrace{\frac{\partial}{\partial v}\left[(a(x)-\eta v)\,p(x,v)\right]}_{\text{drift}} + \underbrace{\frac{\partial}{\partial v}\frac{\partial}{\partial v} D_{vv}\; p(x,v)}_{\text{diffusion}}$$
$$+\frac{\partial}{\partial x}(v\rho)$$



drift: $\frac{d\rho(v)}{dv} = dt \cdot \rho(v+dv)\,\dot{v}(v+dv) - \dot{v}\,\rho(x,v)$