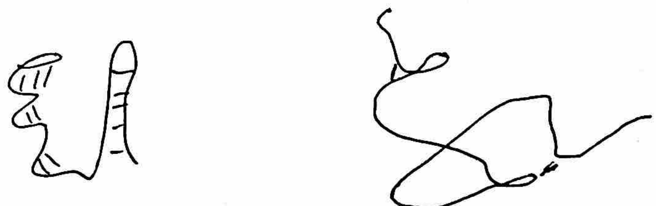
Recap:

In the beginning there was molecular dynamics and a low-dimensional order parameter we wanted to understand

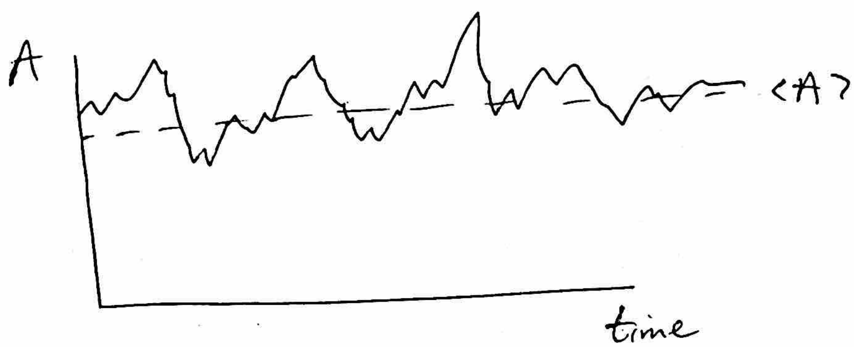
Protein



high A

low A

A = # of native contacts



Time average: $\langle A \rangle = \lim_{T \to \infty} \frac{1}{T} \int_0^T dt\, A(t)$

As $T \to \infty$ all microstates ν have been visited and you should be able to replace the temporal average by a spatial one:

Ensemble average: $\langle A \rangle = \sum_{\nu} P(\nu) A(\nu)$

The ergodic hypothesis said these two are the same

So what is $P(\nu)$?

It depended on the ensemble - which things were conserved with rigid constraints and which ones were allowed to fluctuate

Ensemble	Fixed?	Fluctuating	Thermodynamic Potential	$P(\nu)$
Microcanonical	N, V, E	—	$-S = -k_B \ln \Omega$	$\frac{1}{\Omega}$
Canonical	N, V, T	E	$A = -k_B T \ln Q$	$\frac{e^{-\beta E(\nu)}}{Q}$

~~Two~~ Faces of Q : ① Connection to thermodynamics
② A normalization constant

New15h → $\boxed{3}$ A generating function!

In what way is Q a function? I thought it was a normalization constant.

$$Q(\beta) = \sum_\nu e^{-\beta E(\nu)}$$

$$\left(\frac{\partial Q}{\partial \beta}\right)_{V,N} = \sum_\nu \frac{\partial}{\partial \beta} e^{-\beta E(\nu)} = -\sum_\nu E(\nu)\, e^{-\beta E(\nu)}$$

almost $-\langle E \rangle$ but would have to be $\frac{e^{-\beta E(\nu)}}{Q} = P(\nu)$.

$$\left(\frac{\partial^2 Q}{\partial \beta^2}\right)_{V,N} = -\sum_\nu \frac{\partial}{\partial \beta} E(\nu) e^{-\beta E(\nu)} = \sum_\nu E(\nu)^2 e^{-\beta E(\nu)}$$

almost $\langle E^2 \rangle$, but again we would need a $\frac{1}{Q}$.

What if we instead differentiate $\ln Q$?

$$\left(\frac{\partial \ln Q}{\partial \beta}\right)_{V,N} = \frac{1}{Q}\sum_\nu \frac{\partial}{\partial \beta} e^{-\beta E(\nu)} = -\sum_\nu E(\nu)\frac{e^{-\beta E(\nu)}}{Q}$$

$$= -\sum_\nu E(\nu)\, P(\nu) = -\langle E\rangle .$$

$$\left(\frac{\partial^2 \ln Q}{\partial \beta^2}\right)_{V,N} = \frac{\partial}{\partial \beta}\left[-\frac{1}{Q}\sum_\nu E e^{-\beta E}\right]$$

$$= \frac{1}{Q^2}\frac{\partial Q}{\partial \beta}\sum_\nu E e^{-\beta E} + \frac{1}{Q}\sum_\nu E^2 e^{-\beta E}$$

$$= -\langle E\rangle^2 + \underbrace{\langle E^2\rangle}_{\text{second moment}} = \underbrace{\langle \delta E^2\rangle}_{\text{second cumulant, i.e. variance}}$$

$\boxed{\ln Q \text{ is a "cumulant generating function".}}$

However we could have viewed the second derivative another way...

$$\left(\frac{\partial^2 \ln Q}{\partial \beta^2}\right)_{V,N} = \frac{\partial}{\partial \beta}\left(\frac{\partial \ln Q}{\partial \beta}\right)_{V,N} = \frac{\partial}{\partial \beta}\left(-\langle E\rangle\right)$$

$$= \cancel{\frac{\partial}{\partial \beta}\frac{\partial \beta}{\partial T}}\ \underbrace{\frac{\partial}{\partial T}\frac{\partial T}{\partial \beta}}_{\text{chain rule}}\left(-\langle E\rangle\right)$$

$$= k_B T^2\left(\frac{\partial \langle E\rangle}{\partial T}\right)_{V,N} = k_B T^2 \underbrace{C_V}_{\text{heat capacity}}$$

$$T = \frac{1}{k_B \beta}$$

$$\Rightarrow \frac{dT}{d\beta} = -\frac{1}{k_B \beta^2}$$

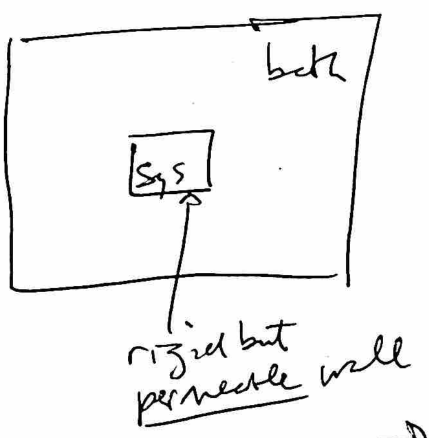
$$= \frac{-1}{1/(T^2 k_B)} = -k_B T^2$$

$$C_V = \underbrace{(k_B T^2)^{-1}}_{\text{a positive \#}} \underbrace{\langle \delta E^2 \rangle}_{\substack{\text{fluctuations in the unperturbed system} \\ \text{(also positive)}}} \geq 0$$

Response of system to a perturbation (change in T) $\rightarrow C_V$

Connection between fluctuations & response is a major theme/triumph in statistical mechanics.

Ensemble	Fixed?	Fluctuating?	Thermodynamic potential?	$P(\nu)$
Grand Canonical	μ, V, T	N, E		



$$E_T = E(\nu) + E_B(\nu_B), \quad N_T = N(\nu) + N_B(\nu_B)$$

$$P(\nu, \nu_B) = \text{const. if } (\nu, \nu_B) \text{ is allowed}$$

$$P(\nu) \propto \Omega_B(E_T - E(\nu), N_T - N(\nu))$$

$$\Rightarrow \ln P(\nu) = \text{const} - E \left(\frac{\partial \ln \Omega_B}{\partial E_B} \right)_{V_B, N_B} - N \left(\frac{\partial \ln \Omega_B}{\partial N_B} \right)_{E_B, V_B}$$

$S_B = \cancel{k_B} \ln \Omega_B$ and $dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN$

$$\Rightarrow \left(\frac{\partial \ln \Omega_B}{\partial E_B} \right)_{V_B, N_B} = \frac{1}{k_B T} \quad \& \quad \left(\frac{\partial \ln \Omega_B}{\partial N_B} \right)_{E_B, V_B} = -\frac{\mu}{k_B T} = -\beta\mu$$

$$\Rightarrow \ln P(\nu) = \text{const.} - \beta E + \beta\mu N \Rightarrow \boxed{P(\nu) \propto e^{-\beta E(\nu) + \beta\mu N}}$$

Normalized by the "grand canonical partition function"

$$\Xi(\beta, V, \beta\mu) = \sum_\nu e^{\beta\mu N - \beta E}$$

$$\Rightarrow \boxed{P(\nu) = \Xi^{-1} e^{-\beta E + \beta\mu N}}.$$

$\ln \Xi$ is also a cumulant generating function

$$\left(\frac{\partial \ln \Xi}{\partial \beta\mu}\right)_{\beta,V} = \frac{1}{\Xi}\frac{\partial}{\partial \beta\mu}\sum_\nu e^{\beta\mu N - \beta E} = \frac{1}{\Xi}\sum_\nu N e^{\beta\mu N - \beta E}$$

$$= \sum_\nu P(\nu) N(\nu) = \langle N \rangle$$

$$\left(\frac{\partial^2 \ln \Xi}{\partial (\beta\mu)^2}\right)_{\beta,V} = \langle \delta N^2 \rangle$$

There's a fluctuation-response relation here too

$$\left(\frac{\partial N}{\partial \beta\mu}\right)_{\beta,V} = N\rho k_B T \kappa_T = \langle \delta N^2 \rangle$$

I haven't shown you all these steps.

Isothermal compressibility $\left(\frac{\partial \rho}{\partial p}\right)_T$

What thermodynamic potential corresponds to $\ln \Xi$?

It is a natural function of $T, \mu,$ + V

$$\Phi \equiv \underset{\substack{\uparrow \\ \text{function of} \\ S, N, V}}{E} - \underset{\substack{\uparrow \\ \text{switch} \\ S \text{ for } T}}{\underbrace{TS}} - \underset{\substack{\text{switch} \\ N \text{ for } \mu}}{\underbrace{\mu N}}$$

$\Leftarrow$ A natural function of $T, \mu,$ + V!