#14 0

1) 2.20b Term Project

Due about RFR week. Fri May 5th Reading & Recitation

Approved Proposal Fri March 24th.

2) Next week - March APS I'm away, so is Aditya.

Guest Lectures

Tue: David Limmer

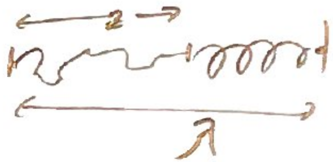
Thr: Steve Whitelam (Molecular Foundry) Self-Assembly.

3) Homework Due Thr 16th March

Hummer - Szabo #1

<u>Hummer - Szabo</u> 2001
2005

$\beta F(z)$ not $\beta F(\lambda)$

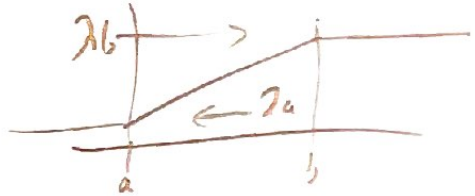


x = internal coordinates of polymer

$E = U(x) + V(z,\lambda)$

$= -\frac{K}{2}(\lambda - z)^2$

Harmonic spring



$$\beta F(z) = -\ln \int dx\, e^{-\beta U(x)}\, \delta(z - z(x))$$

$$= -\ln \int dx\, e^{-\beta E + \beta V}\, \delta(z - z(x))$$

$$= -\ln \left\langle e^{+\beta V}\, \delta(z - z(x)) \right\rangle^{eq}_{\lambda_b}$$

Equilibrium Average at λ_b

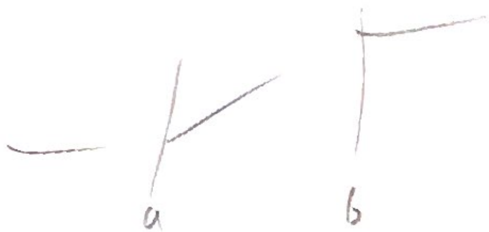
Humm[illegible] #2

2

$$\left\langle f(x_b)\, e^{-\overbrace{\beta W + \beta\Delta F}^{\beta W^{ex}}} \right\rangle_{\Lambda} = \int D[x]\, P(x|\Lambda)\, f(x_b)\, e^{-\beta W^{ex}}$$

$$= \int D[\tilde{x}]\, P(\tilde{x}|\tilde{\Lambda})\, f(\tilde{x}_b)$$

$$= \left\langle f(\tilde{x}_b) \right\rangle_{\tilde{\Lambda}} = \left\langle f(\tilde{x}_b) \right\rangle^{eq} \, !$$



HS

$$\beta F(z) = \ln \left\langle e^{+\beta V - \beta W}\, \delta(z - z(x)) \right\rangle_{\Lambda}$$ [Monte Carlo Connection]

Crooks 2001

$$\underbrace{\ln \left\langle e^{-\beta W} \right\rangle_{\Lambda}} \quad \beta F(\lambda)$$

3

Definitions

change in λ drives away from equilibrium

$$A = -\frac{\partial \beta E}{\partial \lambda} \qquad \delta A = A(t) - \langle A \rangle_{\lambda(t)}$$

"excess" deviation from equilibrium

$$\langle \delta A \rangle_{\lambda}^{eq} = 0$$

$$\beta \Delta E = \beta W + \beta Q$$

$$\underbrace{\beta \int_a^b \frac{\partial E}{\partial \lambda} \frac{\partial \lambda}{\partial t}\, dt}_{\text{work}} + \underbrace{\beta \int \frac{\partial E}{\partial x} \frac{\partial x}{\partial t}\, dt}_{\text{heat}}$$

power

$$\beta P = -A \frac{\partial \lambda}{\partial t} \qquad \delta \beta P = -\frac{\partial \lambda}{\partial t}\, \delta A(t)$$

Linear Response

Kirkwood 1946

$$\langle \delta B(x_b) \rangle_{\Lambda} = \langle e^{-\beta W^{ex}} \delta B(x_b) \rangle_{\tilde{\Lambda}}$$

$$-\beta W^{ex} = \int_b^a \delta A(t) \frac{\partial \lambda}{\partial t} dt$$

$e^x \simeq 1 + x \dots$

$$\overset{LR}{\approx} \langle (-\beta W^{ex}) \delta B(x_b) \rangle_{\tilde{\Lambda}} + \underline{hot}$$

$$\overset{LR}{\approx} \int_b^a \langle \delta A(t) \delta B(x_b) \rangle \frac{\partial \lambda}{\partial t} dt$$

$$\langle \delta B(x_b) \rangle \overset{MCR}{\approx} -\frac{\partial \lambda}{\partial t}\Big|_{\lambda_b} \int_0^\infty \langle \delta A(t) \delta B(0) \rangle^{eq}_{\lambda_b} dt \leftarrow \text{time-correlation function}$$

$$= -\frac{\partial \lambda}{\partial t}\Big|_b \gamma$$

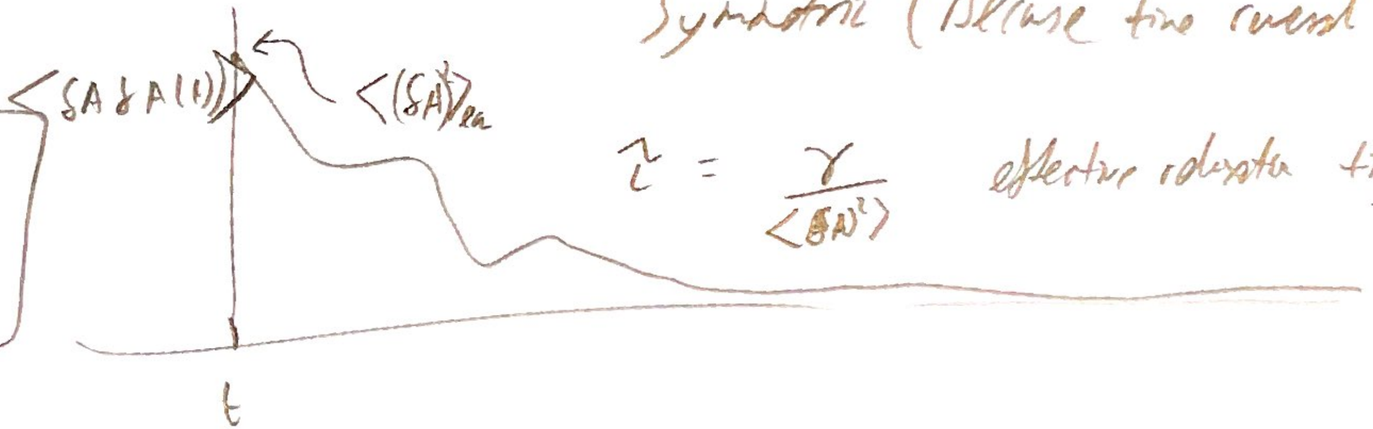
$$\langle \delta\delta P \rangle = -\frac{\partial \lambda}{\partial t} \langle \delta A \rangle_\lambda = +\frac{\partial \lambda}{\partial t}\, \gamma_{AA}\, \frac{\partial \lambda}{\partial t}$$

$$\gamma_{AA} = \int_0^\infty \langle \delta A(0)\, \delta A(t) \rangle^{eq}_\lambda \, dt$$

If many controls $\lambda = \{\lambda_1, \dots \lambda_n\}$, then $A_n = \{-\frac{\partial \Delta E}{\partial \lambda_1}, \frac{\partial \Delta E}{\partial \lambda_1} \dots$

→ γ matrix (positive semidefinite)

Symmetric (Because time reversal symmetry)



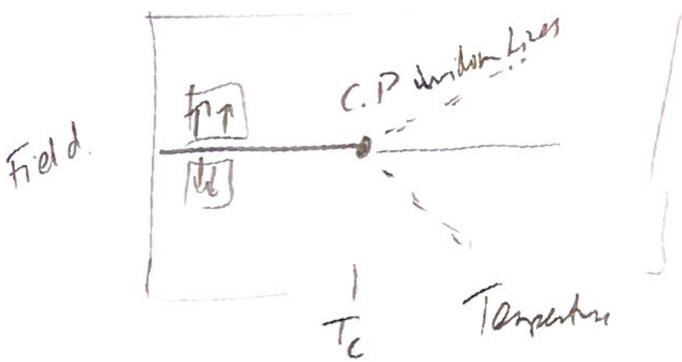
$\tau = \frac{\gamma}{\langle \delta A^2 \rangle}$ effective relaxation time

$\Rightarrow$ Friction is Fluctuations.

2D Ising Model

$$\beta E = -\beta J \sum_{\langle ij \rangle} \sigma_i \sigma_j \quad - \beta h \sum \sigma_j$$

$$M = \sum \sigma_j$$



$$\gamma_{EE} = \tau_{EE}^{eff} \underbrace{\beta^2 \langle \delta E(0) \ \delta E(0) \rangle}_{C_v \text{ heat capacity}}$$

(control Beta & h)

$$\gamma_{EM} = \tau_{EE}^{eff} \langle \delta M(0) \ \delta E(0) \rangle$$

Magneto-caloric coefficient.

(show figures)

Rotskoff 2015