3.2. RW in an External Potential

RW on a lattice, lattice spacing a, 3D, 6 nearest neighbors ($z = 6$)

Start at position $\vec{r}\,'$, end at $\vec{r}$, N bonds, $N+1$ monomers

external potential $U(\vec{r})$, $\frac{U(\vec{r})}{k_B T} \ll 1$

total # of N-step walks: z^N

Def.: Green's function $G_N(\vec{r}', \vec{r})$

based upon $W_N(\vec{r}', \vec{r})$: SET of all the walks with N steps going from $\vec{r}'$ to $\vec{r}$

cancel

$$G_N(\vec{r}', \vec{r}) = \frac{e^{+\beta U(\vec{r}')}}{2^N} \sum_{W_N(\vec{r}', \vec{r})} \exp\left\{-\beta\left[U(\vec{r}') + U(\vec{r}_1) + U(\vec{r}_2) + \dots + U(\vec{r})\right]\right\}$$

walk $\equiv (\vec{r}' \equiv \vec{r}_0, \vec{r}_1, \vec{r}_2, \dots, \vec{r}_N \equiv \vec{r})$

$\beta = 1/(k_B T)$

$U(\vec{r}')$ does <u>not</u> occur

Observations

(i) $U(\vec{r}\,')$ does not occur → for concatenation

(ii) $$\frac{G_N(\vec{r}\,',\vec{r})}{G_N(\vec{r},\vec{r}\,')} = \frac{\exp(\beta U(\vec{r}\,'))}{\exp(\beta U(\vec{r}))} \simeq 1$$

nearly symmetric

(iii) $G_N \geq 0$

(iv) $$G_0(\vec{r}\,',\vec{r}) = \delta_{\vec{r}\,',\vec{r}} = \begin{cases} 1 & \vec{r}\,' = \vec{r} \\ 0 & \text{else} \end{cases}$$

(v) "gauge invariance" $U(\vec{r}) \to U(\vec{r}) + \Delta U$

constant offset

$$G_N \to G_N \exp(-\beta N \Delta U)$$

$\Rightarrow G_N$ cannot be measurable!

similar to partition function!

(vi) Composition law

$$\sum_{\vec{s}'} G_{N'}(\vec{r}', \vec{s})\, G_{N-N'}(\vec{s}, \vec{r}) =$$

$$\frac{1}{z^{N'}} \frac{1}{z^{N-N'}} \sum_{\vec{s}} \sum_{W_{N'}(\vec{r}', \vec{s})} \sum_{W_{N-N'}(\vec{s}, \vec{r})}$$

$$\boxed{\vec{r}_N \equiv \vec{r}}$$

$$\exp\left(-\beta\left[U(\vec{r}_1) + U(\vec{r}_2) + \ldots + U(\vec{s})\right]\right)$$

$$\exp\left\{-\beta\left[U(\vec{r}_{N'+1}) + U(\vec{r}_{N'+2}) + \ldots + U(\vec{r}_N)\right]\right\} =$$

$$\frac{1}{z^N} \sum_{W_N(\vec{r}', \vec{r})} \exp\left[-\beta \left(u(\vec{r}_1) + u(\vec{r}_2) + \ldots + u(\vec{r})\right)\right]$$

$$= G_N(\vec{r}', \vec{r})$$

$$\boxed{G_N(\vec{r}', \vec{r}) = \sum_{\vec{s}} G_{N'}(\vec{r}', \vec{s})\, G_{N-N'}(\vec{s}, \vec{r})}$$

(vii) $$G_1(\vec{r}\,', \vec{r}) = \frac{1}{z} \exp\left[-\beta U(\vec{r})\right]$$

for $|\vec{r} - \vec{r}\,'| = a$, zero otherwise

$$\Rightarrow G_{N+1}(\vec{r}\,', \vec{r}) = \sum_{\vec{s} \in nn(\vec{r})} G_N(\vec{r}\,', \vec{s})\, G_1(\vec{s}, \vec{r})$$

$$= \frac{1}{z} \exp\left[-\beta U(\vec{r})\right] \sum_{\vec{s} \in nn(\vec{r})} G_N(\vec{r}\,', \vec{s})$$

G_N varies slowly

$$G_N(\vec{r}',\vec{s}) \simeq G_N(\vec{r}',\vec{r}) + \frac{\partial G_N}{\partial \vec{r}}(\vec{s}-\vec{r})$$

$$+ \frac{1}{2}\sum_{\alpha\beta} \frac{\partial^2 G_N}{\partial r_\alpha \partial r_\beta}(s^\alpha - r^\alpha)(s^\beta - r^\beta) + \dots \Bigg| \sum_{\vec{s}\in nn(\vec{r})}$$

α,β: Cartesian indices

$$\sum_{\vec{s}\in nn(\vec{r})} G_N(\vec{r}',\vec{s}) \cong z\, G_N(\vec{r}',\vec{r}) + \frac{1}{2}\sum_{\alpha\beta}\frac{\partial^2 G_N}{\partial r_\alpha \partial r_\beta} A\,\delta_{\alpha\beta} + \dots$$

$$\sum_{\vec{s} \in nn(\vec{r})} (s^\alpha - r^\alpha)(s^\beta - r^\beta) = A\, \delta_{\alpha\beta}$$

for symmetry reasons

$A = ?$ trace:

$$\sum_{\vec{s} \in nn(\vec{r})} \underbrace{(\vec{s} - \vec{r})^2}_{a^2} = A \cdot 3$$

$$z\, a^2 = 3A \quad \Rightarrow \quad A = \frac{z a^2}{3}$$

$$\sum_{\vec{s} \in nn(\vec{r})} G_N(\vec{r}\,', \vec{s}) \simeq z\, G_N(\vec{r}\,', \vec{r}) + \frac{z a^2}{6} \sum_{\alpha\beta} \frac{\partial^2 G_N}{\partial r_\alpha \partial r_\beta} \delta_{\alpha\beta} + \ldots$$

$$\simeq z\, G_N(\vec{r}', \vec{r}) + \frac{z a^2}{6} \nabla_r^2 G_N(\vec{r}', \vec{r}) + \ldots$$

$$e^{-\beta u} \simeq 1 - \beta u \qquad (u \ll k_B T)$$

$(\beta u)(\nabla^2 G) \cdot \frac{a^2}{6}$ small of 2nd order
discard

$$G_{N+1}(\vec{r}', \vec{r}) \simeq G_N(\vec{r}', \vec{r}) - \beta u\, G_N(\vec{r}', \vec{r})$$

$$+ \frac{a^2}{6} \nabla^2 G_N(\vec{r}', \vec{r})$$

$$G_N(\vec{r}\,',\vec{r}) - G_{N+1}(\vec{r}\,',\vec{r}) =$$

$$= -\frac{a^2}{6}\nabla^2 G_N(\vec{r}\,',\vec{r}) + \beta u\, G_N(\vec{r}\,',\vec{r})$$

$$\boxed{-\frac{\partial}{\partial N} G_N = \left[-\frac{a^2}{6}\nabla^2 + \beta u\right] G_N} \quad (*)$$

solve this with initial condition

$$G_0(\vec{r}\,',\vec{r}) = a^3\,\delta(\vec{r}\,'-\vec{r})$$

$$i\hbar \frac{\partial}{\partial t} \Psi = \left[-\frac{\hbar^2}{2m} D^2 + U \right] \Psi$$

Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \longrightarrow -\frac{\partial}{\partial N}$$ imaginary time

$$\frac{\hbar^2}{2m} \longrightarrow \frac{a^2}{6}$$

$$U \longrightarrow \beta U$$

How to calculate physical properties from G?

volume fraction $\phi(\vec{s}) \equiv$ mean occupation of site $\vec{s}$

$$\phi(\vec{s}) = \frac{\sum_{\vec{r}'} \sum_{\vec{r}} \sum_{N'=0}^{N} G_{N'}(\vec{r}', \vec{s})\, G_{N-N'}(\vec{s}, \vec{r})}{\sum_{\vec{r}'} \sum_{\vec{r}} G_N(\vec{r}', \vec{r})}$$

$\sum_{\vec{s}} \phi(\vec{s}) = N+1$ correctly normalized

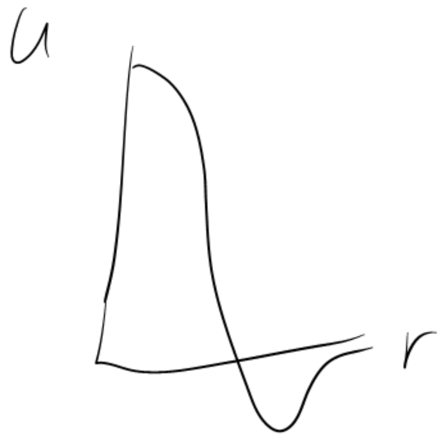
ambiguity ("gauge invariance") cancels out.

3.3. Many Non-Interacting RWs in an External Potential

Precisely as before. At the end, we have to multiply $\mathcal{D}(\bar{s})$ with the # of chains!

3.4. SCFT for Many-Chain Systems

Consider N particles interacting via potential $U(\vec{r})$. For convenience, assume $U(0)$ finite



$$\mathcal{H} = \sum_{i<j} U(\vec{r}_i - \vec{r}_j) =$$

$$= \frac{1}{2} \sum_{i,j} U(\vec{r}_i - \vec{r}_j) - \frac{1}{2} N U(0) =$$

$$= -\frac{1}{2} N U(0) + \frac{1}{2} \sum_{i,j} \int d^3\vec{r} \int d^3\vec{r}\,' \, \delta(\vec{r} - \vec{r}_i)\, \delta(\vec{r}\,' - \vec{r}_j) \, U(\vec{r} - \vec{r}\,')$$

Define $c(\vec{r}) = \sum_i \delta(\vec{r} - \vec{r}_i)$

$$\mathcal{H} = -\frac{N}{2} U(0) + \frac{1}{2} \int d^3\vec{r} \int d^3\vec{r}\,' \, U(\vec{r} - \vec{r}\,') \, c(\vec{r}) \, c(\vec{r}\,')$$

<u>Mean Field Approximation:</u>

$$c(\vec{r}) = \langle c(\vec{r}) \rangle + \delta c(\vec{r})$$

$$c(\vec{r}) \, c(\vec{r}\,') = \langle c(\vec{r}) \rangle \langle c(\vec{r}\,') \rangle +$$

$$+ \langle c(\vec{r}) \rangle \, \delta c(\vec{r}\,') + \langle c(\vec{r}\,') \rangle \, \delta c(\vec{r})$$

$$+ \underbrace{\delta c(\vec{r}) \, \delta c(\vec{r}\,')}_{} \rightarrow \text{DISCARD}$$

omit constant offsets:

$$\mathcal{H}_{MF} = \frac{1}{2} \int d^3\vec{r} \int d^3\vec{r}\,' \; U(\vec{r} - \vec{r}\,') \left\{ \langle c(\vec{r}) \rangle \, \delta c(\vec{r}\,') + \langle c(\vec{r}\,') \rangle \, \delta c(\vec{r}) \right\}$$

<u>Define:</u> effective potential

$$V(\vec{r}) = \int d^3\vec{r}\,' \; \langle c(\vec{r}\,') \rangle \, U(\vec{r} - \vec{r}\,')$$

$$\Rightarrow \mathcal{H}_{MF} = \int d^3\vec{r} \; V(\vec{r}) \, \delta c(\vec{r})$$

add a constant offset:

$$\mathcal{H}_{MF} = \int d^3\vec{r}\; V(\vec{r})\, c(\vec{r}) = \sum_i V(\vec{r}_i)$$

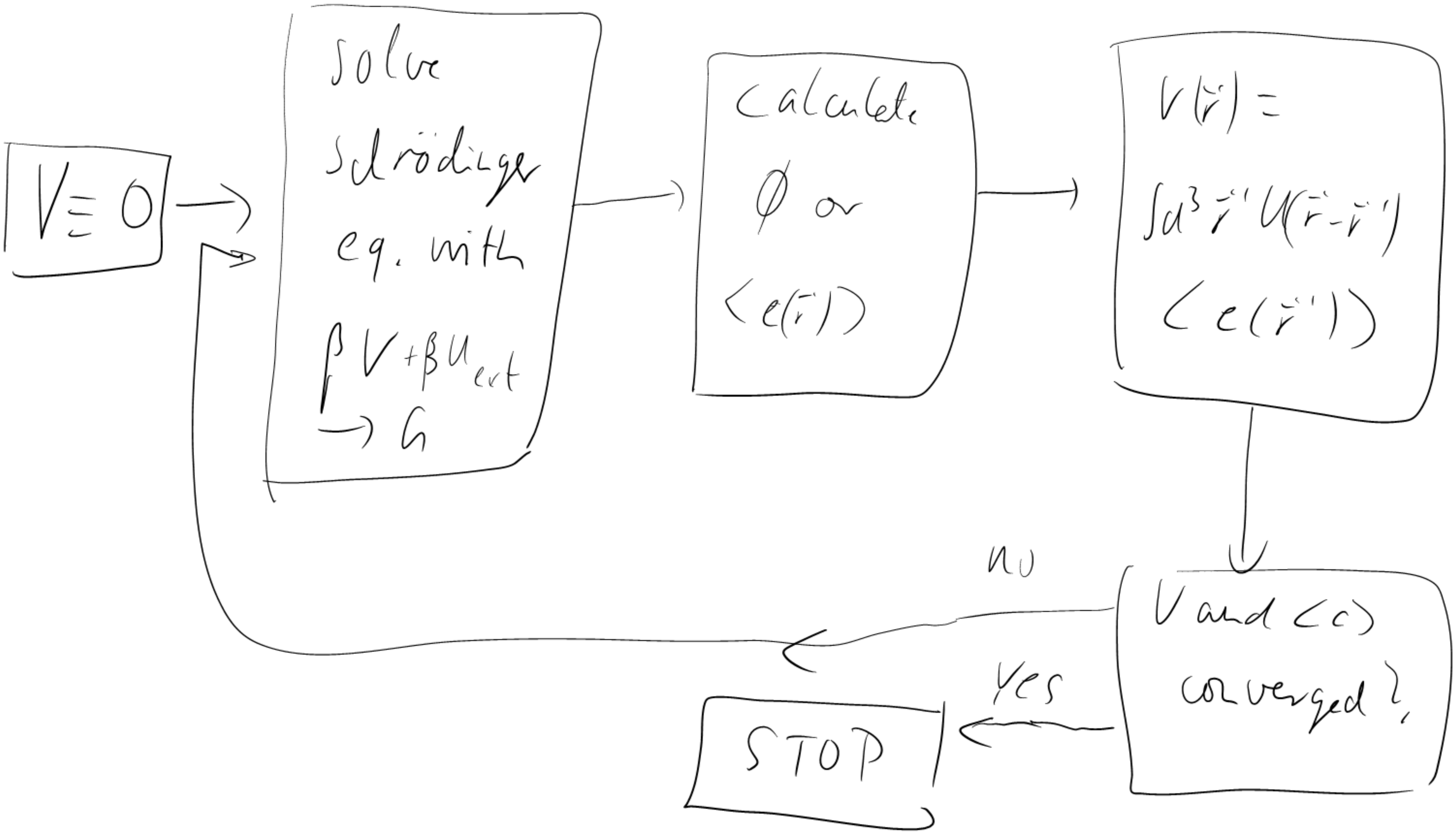
$$V(\vec{r}) = \int d^3\vec{r}\,'\; U(\vec{r}-\vec{r}\,')\langle c(\vec{r}\,')\rangle$$

"external" potential

with real external potential U_{ext}

$$\mathcal{H}_{MF} = \sum_i \left[V(\vec{r}_i) + U_{ext}(\vec{r}_i) \right]$$

SCFT for polymer systems



Flory Theorem

Consider <u>dense</u> homogeneous melt of polymers

density high → fluctuations of density (polymer density) should be small → SCFT should work

→ $\langle c(\vec{r}) \rangle = \text{const}$

→ $V(\vec{r}) = \text{const.}$

→ Schrödinger eq. in constant potential

→ " " " ZERO "

→ " " for the <u>free</u> random walk

→ chain conformations are RW-like

<u>or</u>: In dense polymer systems, excluded volume interactions are <u>SCREENED</u>