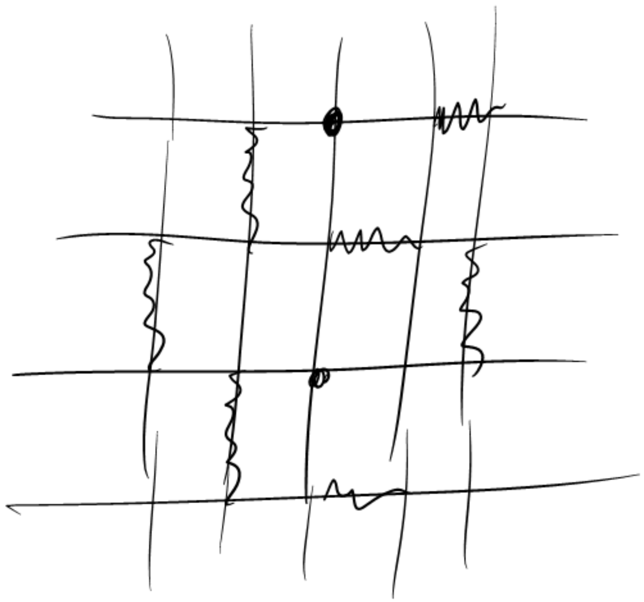
Where does Flory screening come from?

<u>de Gennes:</u> Consider two monomers

in a system of dimers



requirement: each site

is occupied at most once

~~ : dimers

• monomers

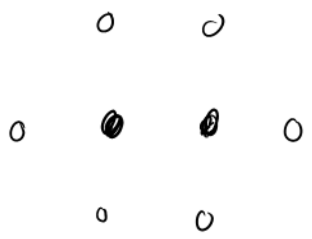
Situation 1: monomers far away from each other

• monomer

o blocked site

total # of blocked sites: 8

Situation 2: Monomers on nearest-neighbor sites



blocked sites: 6

entropically favored → dimers have more configuration space

→ attraction due to entropic packing effects

→ compensates the swelling

"A swollen chair would take too much configuration space from its neighboring fellow chairs!"

3.6. Excursion: The Diffusion Equation

$$\frac{\partial}{\partial t} P(\vec{r}, t) = D \, \nabla^2 P(\vec{r}, t)$$

time derivative

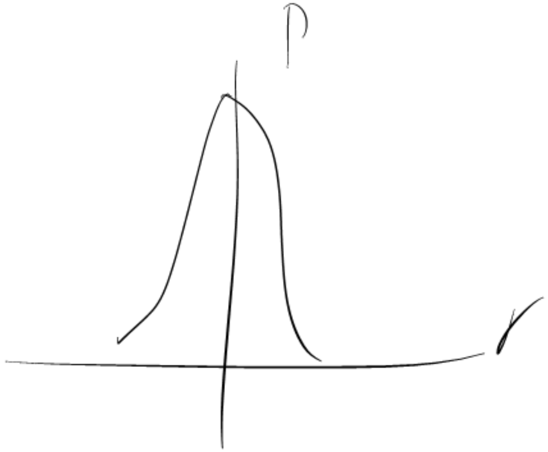
density probability

diffusion constant

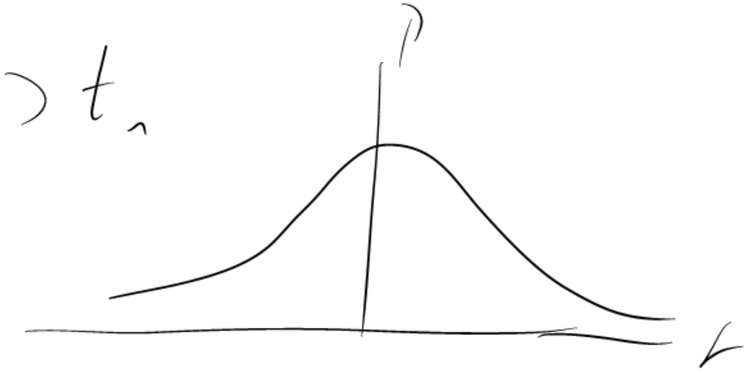
$$P(\vec{r}, t=0) = \delta(\vec{r})$$

$t = 0$

$t_1 > 0$:



$t_2 > t_1$



$$\tilde{P}(\vec{k},t) = \int d^3\vec{r}\; P(\vec{r},t)\, \exp(-i\vec{k}\cdot\vec{r})$$

$$P(\vec{r},t) = \frac{1}{(2\pi)^3} \int d^3\vec{k}\; \tilde{P}(\vec{k},t)\, \exp(+i\vec{k}\cdot\vec{r})$$

$$\nabla^2 P(\vec{r},t) = \frac{1}{(2\pi)^3} \int d^3\vec{k}\; \tilde{P}(\vec{k},t)\left(-\vec{k}^2\right) \exp(i\vec{k}\cdot\vec{r})$$

$$\frac{\partial}{\partial t} P(\vec{r},t) = \frac{1}{(2\pi)^3} \int d^3\vec{k} \left[\frac{\partial}{\partial t}\tilde{P}\right] \exp(i\vec{k}\cdot\vec{r})$$

$$\frac{\partial}{\partial t} \tilde{P}(\vec{k}, t) = -D \vec{k}^2 \tilde{P}(\vec{k}, t)$$

$$\tilde{P}(\vec{k}, t=0) = \int d^3\vec{r}\; P(\vec{r}, t=0) \exp(-i \vec{k} \cdot \vec{r})$$

$$= \int d^3\vec{r}\; \delta(\vec{r}) \exp(-i \vec{k} \cdot \vec{r}) =$$

$$= 1$$

$$\tilde{P}(\vec{k}, t) = \exp\left[-D \vec{k}^2 t\right]$$

$$P(\vec{r},t) = \frac{1}{(2\pi)^3} \int d^3\vec{k} \; \exp\left[-D\vec{k}^2 t + i\vec{k}\cdot\vec{r}\right] =$$

$$= \ldots = (4\pi D t)^{-3/2} \exp\left(-\frac{\vec{r}^2}{4Dt}\right)$$

$$\langle x^2 \rangle = 2Dt$$

$$\langle y^2 \rangle = 2Dt$$

$$\langle z^2 \rangle = 2Dt$$

$$\langle \vec{r}^2 \rangle = 6Dt$$

3.7. Schrödinger Eq. with Constant Potential

$$\frac{\partial}{\partial N} G_N(\vec{r}) = \left[\frac{a^2}{6} D^2 - \underbrace{\beta u}_{\text{const.}}\right] G_N(\vec{r})$$

$(\vec{r}\,' = 0)$

First: $u = 0$

$N \longleftrightarrow t$

$\frac{a^2}{6} \longleftrightarrow D$

$$\boxed{\begin{array}{c}\text{init. cond.:}\\ G_0(\vec{r}) = a^3 \delta(\vec{r})\end{array}}$$

$$G_N(\vec{r}) = a^3 \left[4\pi \frac{a^2}{6} N\right]^{-3/2} \exp\left[-\frac{\vec{r}^{\,2}}{4\frac{a^2}{6}N}\right]$$

$$= \left(\frac{2}{3}\pi N\right)^{-3/2} \exp\left(-\frac{3\vec{r}^{\,2}}{2Na^2}\right)$$

now, <u>with</u> potential (but constant): <u>CLAIM:</u>

$$G_N(\vec{r}) = \underbrace{\left(\frac{2}{3}\pi N\right)^{-3/2} \exp\left(-\frac{3\vec{r}^{\,2}}{2Na^2}\right)}_{G_N^{(0)}(\vec{r})} \exp(-\beta U N)$$

$$\frac{\partial}{\partial N} G_N(\bar{r}) = \left[\frac{\partial}{\partial N} G_N^{(0)}(\bar{r})\right] \exp(-\beta u N)$$

$$+ \quad G_N^{(0)}(\bar{r}) \frac{\partial}{\partial N} \exp(-\beta u N) =$$

$$= \frac{a^2}{6}\left[\nabla^2 G_N^{(0)}(\bar{r})\right] \exp(-\beta u N)$$

$$+ \quad G_N^{(0)}(\bar{r}) (-\beta u) \exp(-\beta u N) =$$

$$= \frac{a^2}{6} \nabla^2 \left[G_N^{(0)}(\bar{r}) \exp(-\beta u N)\right] - \beta u \, G^{(0)}(\bar{r}) \exp(-\beta u N)$$

$$=$$

$$= \left[\frac{a^2}{6}\nabla^2 - \beta U\right]\left[G_N^{(0)}(\vec{r}) \exp(-\beta U N)\right]$$

$$= \left[\frac{a^2}{6}\nabla^2 - \beta U\right] G_N(\vec{r})$$

Now, consider <u>one</u> RW in a box of volume V, constant potential U

linear size of box $\gg R_G$ (chain)

Partition function Z

$$Z = [\text{sum of all Boltzmann factors}]$$

$$= \sum_{\vec{r}', \vec{r}} G_N(\vec{r}', \vec{r}) = \text{continuum limit}$$

$$= \frac{1}{a^6} \int d^3\vec{r}' \int d^3\vec{r} \underbrace{G_N(\vec{r}', \vec{r})}_{= G_N(\vec{r} - \vec{r}')} =$$

$$= \frac{V}{a^6} \int d^3\vec{r}\, G_N(\vec{r}) =$$

$$= \frac{V}{a^6} \exp[-\beta u N] \underbrace{\int d^3\vec{r}\, G_N^{(0)}(\vec{r})}_{a^3} = \frac{V}{a^3} \exp(-\beta u N)$$

excursion

$\vec{z} = \vec{r} - \vec{r}\,' \quad \vec{r} = \vec{z} + \vec{r}\,'$

$$\int d^3\vec{r}\,' \int d^3\vec{r} \; G(\vec{r} - \vec{r}\,') =$$

$d^3\vec{r} = d^3\vec{z}$

$\vec{z} \to \vec{r}$

$$= \int d\vec{r}\,' \int d^3\vec{z} \; G(\vec{z}) = V \int d^3\vec{z} \; G(\vec{z}) =$$

$$= V \int d^3\vec{r} \; G(\vec{r})$$

$$Z = \exp[-\beta u N] \frac{V}{a^3}$$

Free energy: $F = -k_B T \ln Z =$

$$= \underbrace{-k_B T \ln \frac{V}{a^3}}_{\text{translational entropy}} + \underbrace{uN}_{\text{energy}}$$

Now, M non-interacting RWs again in the box of size V

$$F = -k_B T \ln\left\{\frac{1}{M!}\left[\frac{V}{a^3}\exp(-\beta U N)\right]^M\right\} =$$

$$+ k_B T \ln M! - k_B T M \ln\left\{\frac{V}{a^3}\exp(-\beta U N)\right\} =$$

$$= k_B T \ln M! + M\left\{UN - k_B T \ln\frac{V}{a^3}\right\} =$$

$$= k_B T \ln M! + UMN - M k_B T \ln\frac{V}{a^3}$$

Stirling: $\ln M! \simeq M \ln M - M \qquad M \to \infty$

$$F = k_B T \left[M \ln M - M \right] + UMN - M k_B T \ln \frac{V}{a^3} =$$

$$= UMN - M k_B T + M k_B T \ln \frac{M a^3}{V} \qquad \Big| \cdot \frac{a^3}{V}$$

volume fraction: $\phi = \dfrac{MNa^3}{V} \Rightarrow \dfrac{Ma^3}{V} = \dfrac{\phi}{N}$

free energy per lattice site: $f = \dfrac{F a^3}{V}$

$$\boxed{f = U \phi - k_B T \frac{\phi}{N} + k_B T \frac{\phi}{N} \ln \frac{\phi}{N}}$$

3.8. Flory-Huggins Theory for Polymer Mixtures

Type A, type B : N_A chain length A

N_B " " B

ϕ_A : volume frac. A

ϕ_B : " " B

$$\left.\begin{array}{l}\phi_A \\ \phi_B\end{array}\right\} \quad \phi_A + \phi_B = 1$$

$$\phi_B = 1 - \phi_A = 1 - \phi$$

$$\phi_A \equiv \phi$$

<u>single</u> variable ϕ

interaction is hidden in the self-consistent potential (spatially constant)

$$f = U_A \phi_A - k_B T \frac{\phi_A}{N_A} + k_B T \frac{\phi_A}{N_A} \ln \frac{\phi_A}{N_A}$$

$$+ U_B \phi_B - k_B T \frac{\phi_B}{N_B} + k_B T \frac{\phi_B}{N_B} \ln \frac{\phi_B}{N_B}$$

$$U_A = u_{AA} \phi_A + u_{AB} \phi_B \quad \Big| \cdot \phi_A$$

$$U_B = u_{AB} \phi_A + u_{BB} \phi_B \quad \Big| \cdot \phi_B$$

exclusion : single

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

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

two : $(A + B)$

$$V_A = U_{AA} \langle c_A \rangle + U_{AB} \langle c_B \rangle$$

$$u_A \phi_A + u_B \phi_B =$$

$$= u_{AA} \phi_A^2 + u_{BB} \phi_B^2 + 2 u_{AB} \phi_A \phi_B =$$

$$= u_{AA} \phi_A (1 - \phi_B) + u_{BB} \phi_B (1 - \phi_A) + 2 u_{AB} \phi_A \phi_B =$$

$$= (2 u_{AB} - u_{AA} - u_{BB}) \phi_A \phi_B + \underbrace{u_{AA} \phi_A + u_{BB} \phi_B}_{\text{linear in } \phi}$$

<u>Def.:</u> $\chi := \frac{1}{k_B T}\left(2u_{AB} - u_{AA} - u_{BB}\right)$

Flory interaction parameter

$$\boxed{\frac{f}{k_B T} = \frac{\phi_A}{N_A}\ln\frac{\phi_A}{N_A} + \frac{\phi_B}{N_B}\ln\frac{\phi_B}{N_B} + \chi\,\phi_A\,\phi_B}$$

$+$ const. $+$ linear in ϕ

$\downarrow$

do not matter for the phase behavior