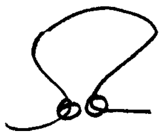
Chem 664
Handout #9

10/21/02

Chapter 3 - Real Chains

- Isolated chain
- Ideal chain - no interaction among monomers
- Real chain - interactions among monomers because they are immersed in solvents

What is the probability for monomer - monomer contact within an isolated chain?



Mean field estimate:

1) Overlap volume fraction in d-dimension

$$\phi^* = b^d N / R^d$$

2) Random flight (Gaussian) chain in any d

$$R = bN^{1/2}$$

$$\therefore \phi^* = \cancel{b^d} N / \cancel{b^d} N^{d/2} \approx N^{1-\frac{d}{2}}, \quad \phi^* \approx N^{1-\frac{d}{2}} << 1$$

for $d > 2$ & $N >> 1$

$$\phi^* \approx 1/\sqrt{N} << 1$$

for $d = 3$ & $N >> 1$

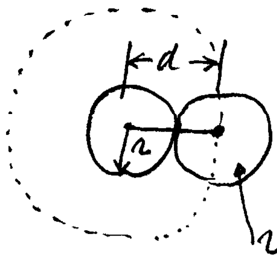
For $d = 3$, monomer-monomer contacts within an isolation chain:

$$N\phi^* \simeq N^{1/2} >> 1 \quad \text{if } N >> 1 \text{ whereas } \phi^* << 1$$

For $d = 4$, $N\phi^* = N^{2-2} = N^0$

For $d > 4$, $N\phi^* << 1$ if $N >> 1$

Excluded volume effect & Self-Avoiding Walks (SAW)



excluded volume for a pair of molecules with hard-core repulsive interactions
$= 8v_0 = \frac{4\pi}{3}d^3$

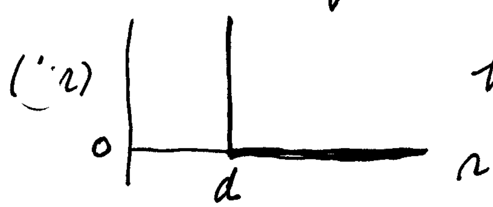
Hence, the excluded volume per molecule
$v = 4v_0 \approx d$

Intermonomer potential $U(r)$, Boltzmann factor $e^{-U(r)/kT}$
& Mayer-f function

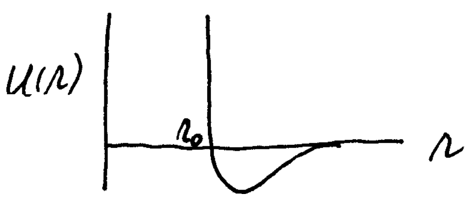
$$f(\underline{r}) \equiv e^{-U(\underline{r})/kT} - 1$$

Formal definition of excluded volume

$$v \equiv -\int_V f(\underline{r})\,d\underline{r} = \int_V [1 - e^{-U(\underline{r})/kT}]\,d\underline{r}$$



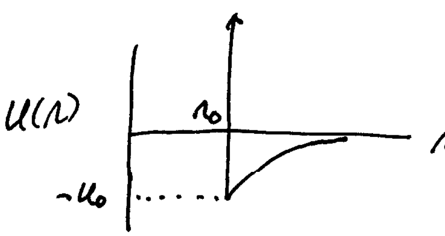
hard-core repulsive

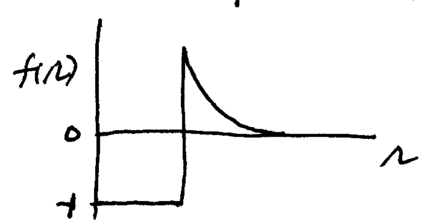


Probability for pairwise contact $\propto e^{-U(r)/kT}$

≈ 0 at $r < r_0$
> 0 at $r > r_0$
≈ 1 at $r >> r_0$

$f(\underline{r}) = 0$ as $r \to \infty$
$f(\underline{r} < r_0) < 0$
$f(\underline{r} > r_0) > 0$





$U(r) = \infty$, $0 \le r \le r_0$
$U(r) = -u_0\left(\frac{r_0}{r}\right)^m$
$r_0 < r \le \infty$

vdW gas

$$\frac{P\bar{V}}{RT} = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{\bar{V}} + \dots$$
$$\approx 1 + \left(b - \frac{a}{RT}\right)\frac{1}{\bar{V}}$$

$$P = \frac{kT}{v_0}\left(1 - \frac{\beta}{2v_0}\right), \quad \frac{\beta}{2} = \frac{a}{kT} - b$$
$$= \frac{kT}{v_0}\left[1 + \left(\frac{a}{kT} - b\right)\frac{1}{v_0}\right]$$

$$\beta \equiv 4\pi\int_0^\infty r^2\left(e^{-U(r)/kT} - 1\right)dr$$
$$= \int f(\underline{r})\,d\underline{r}$$

Cluster Integral

Net repulsive interaction, $v > 0$
Net attractive ″ , $v < 0$

Ignore aspect ratio of monomer shape

Virial expansion of interaction component of Helmholtz free energy,

$$\frac{A_{int}}{V} \approx kT(\underbrace{v\, C_n^2}_{\text{binary monomer-monomer interactions}} + \underbrace{w\, C_n^3}_{\text{ternary monomer-monomer interactions}} + \dots)$$

C_n = number density of monomer

$C_n^2 \approx N^2/R^6$

$C_n^3 \approx N^3/R^9$

Measures of monomer-solvent interactions, v

A) Athermal solution, hard-core potential only

$$v = \int_V [1 - e^{-u(r)/kT}]\, dr \approx \int_V dr \approx b^3$$

$T\uparrow,\ e^{-u(r)/kT} \to 0$

B) Good solvent, predominant repulsive potential

$0 < v < b^3$

C) Theta solvent/temp, net interaction is zero

$v = 0$ PS, $\theta = 34.5°C$ in cyclohexane

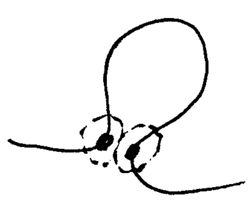
D) Poor solvent, net attractive potential

$-b^3 < v < 0$

E) Non-solvent

$v \approx -b^3$

Chain swelling due to the excluded volume effect:



$$A_{int}/\text{monomer} = \underbrace{kT}_{\text{thermal energy}} \cdot \underbrace{v}_{\text{excluded vol/monomer}} \cdot \underbrace{\frac{N}{R^3}}_{\text{\# density of monomer}}$$

Total Helmholtz free energy = interaction + chain entropy

$$A = A_{int} + A_{ent} = \underbrace{A_e + A_s}_{\text{different notations}} = kT\frac{N^2 v}{R^3} + kT\frac{R^2}{Nb^2}$$

R: swollen linear dimension

$$A = kT\left(\frac{N^2 v}{R^3} + \frac{R^2}{Nb^2}\right)$$

$R > R_0 = N^{1/2} b$

At equilibrium when the swelling reaches its equilibrium value, R_F

$$\left(\frac{\partial A}{\partial R}\right) = 0 = kT\left(-\frac{3N^2 v}{R^4} + \frac{2R}{Nb^2}\right), \quad \frac{3vN^2}{R_F^4} = \frac{2R_F}{Nb^2}$$

$$R_F^5 = \frac{3vN^2}{2}\cdot Nb^2 \approx v b^2 N^3,$$

$$\boxed{R_F \approx v^{1/5} b^{2/5} N^{3/5}},$$

$$R_F/R_0 = v^{1/5} b^{-3/5} N^{1/10} = \left(\frac{v}{b^3}N^{1/2}\right)^{1/5} > 1$$

if $\frac{v}{b^3}N^{1/2} > 1$

if $\frac{v}{b^3}N^{1/2} < 1$, $R_F/R_0 = 1$

Chain interaction parameter

$$z \equiv \left(\frac{3}{2\pi}\right)^{3/2}\frac{v}{b^3}N^{1/2} \approx \frac{A_e(R_0)}{kT} \approx \frac{N^2 v}{(Nb^2)^{3/2}} \approx \frac{v}{b^3}N^{1/2}$$

$z > 1$, Chain swelling

$z < 1$, no chain swelling

$R_F \sim N^{3/5}$, $R_0 \sim N^{1/2}$,

$R \sim N^{\nu}$, $D = 1/\nu$, $\begin{cases} 2 & \text{ideal chain} \\ 5/3 & \text{real chain (swollen)} \end{cases}$

fractal dimension

Tension blob

Ideal	Real	Remarks
$R_0 \approx b N^{1/2}$	$R_F \approx b N^{3/5}$	
$r \approx b n^{1/2}$	$r \approx b n^{3/5}$	self-similar
$\xi \approx b g^{1/2}$	$\xi \approx b g^{3/5}$	
$R_f \approx \xi \frac{N}{g} \approx \frac{Nb^2}{\xi} \approx \frac{R_0^2}{\xi}$	$R_f \approx \xi \frac{N}{g} \approx \xi \frac{Nb^{5/3}}{\xi^{5/3}} \approx \frac{R_F^{5/3}}{\xi^{2/3}}$	tension dimension
$\xi \approx R_0^2 / R_f$	$\xi \approx \frac{R_F^{5/2}}{R_f^{3/2}}$	tension blob
$A(N, R_f) \approx kT \frac{N}{g} \approx kT \frac{R_f}{\xi} \approx kT \left(\frac{R_f}{R_0}\right)^2$	$A(N, R_f) \approx kT \frac{N}{g} \approx kT \frac{R_f}{\xi} \approx kT \left(\frac{R_f}{R_F}\right)^{5/2}$	Free energy cost for tension
$f = \frac{kT}{\xi} \approx kT \frac{R_f}{R_0^2} \approx \frac{kT}{R_0} \left(\frac{R_f}{R_0}\right)$	$f = \frac{kT}{\xi} \approx kT \frac{R_f^{3/2}}{R_F^{5/2}} \approx \frac{kT}{R_F} \left(\frac{R_f}{R_F}\right)^{3/2}$	