Ch 04
Basic forces

Electromagnetic forces

$$F = -\frac{dW}{dr}$$

- Steric (excluded volume)
- Van der Waals
- Electrostatic
- Hydrogen bonding
- hydrophilic

Steric - hard spheres

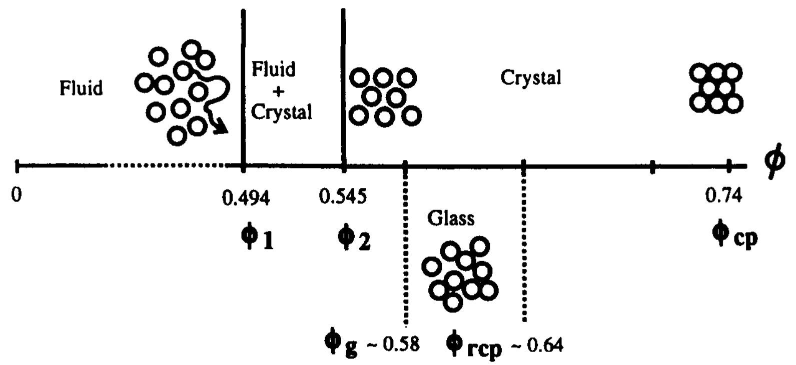


Figure 2.1 The hard-sphere phase diagram. Below volume fraction $\phi < \phi_1 = 0.494$, the suspension is a disordered fluid. Between $\phi_1 = 0.494$ and $\phi_2 = 0.545$, there is coexistence of this disordered phase with a colloidal crystalline phase with FCC (or HCP) order; the colloidal crystalline phase is the equilibrium one up to the maximum close-packing limit of $\phi_{cp} = 0.74$. Nonequilibrium colloidal "glassy" behavior can also occur between $\phi_g = 0.58$ and the limit of random close packing at $\phi_{rcp} = 0.64$. (From Poon and Pusey, fig. 5, with kind permission of Kluwer Academic Publishers, Copyright 1995.)

The hard sphere crystal transition is driven by entropy.

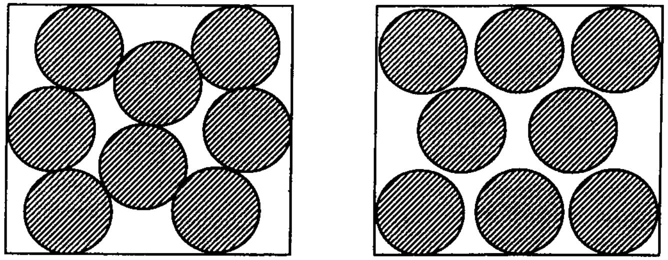


Figure 2.2. In **(a)** and **(b)**, the same number of spheres of the same size are packed into the same space. The disordered sphere packing in **(a)** can create more "free volume" by ordering into a regular packing in **(b)**, thereby creating volume entropy while losing configurational entropy (after Lekkerkerker, unpublished). (From Poon and Pusey, fig. 4, with kind permission of Kluwer Academic Publishers, Copyright 1995.)

Steric – nematic phase

The degree of orientation order is described by an orientational order parameter S

$$S = \tfrac{3}{2}\left\langle \cos^2\theta \right\rangle - \tfrac{1}{2} \qquad \left\langle \cdot \right\rangle \equiv \int \cdot\, \psi(\mathbf{u})\, du^2 \equiv \int_0^{\pi} \int_0^{2\pi} \cdot\, \psi(\mathbf{u})\, d\phi \sin\theta\, d\theta$$

Onsager theory

$$V_{nem}(\mathbf{u}) = V_0(\mathbf{u}) = U_0 k_B T \int \psi(\mathbf{u}') \sin(\mathbf{u}', \mathbf{u})\, du'^2$$

$$\psi(\mathbf{u}) = C e^{-V_{nem}(\mathbf{u})/k_B T}$$ Boltzmann distribution

Maier-Saupe theory

$$V_{nem}(\mathbf{u}) = V_{MS}(\mathbf{u}) \equiv const - \tfrac{3}{2} u_{MS} \mathbf{uu} : \mathbf{S} \qquad \mathbf{S} \equiv \left\langle \mathbf{uu} \right\rangle - \tfrac{1}{3} \boldsymbol{\delta}$$

Can be solved by a self-consistent calculation

Steric – freely jointed chain

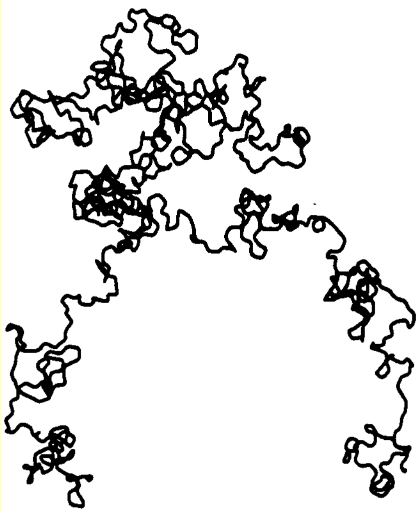


Figure 2.8 Random walk formed from 1000 links. (From Treloar, copyright © 1975 by Oxford University Press, Inc. Used by permission of Oxford University Press, Inc.)

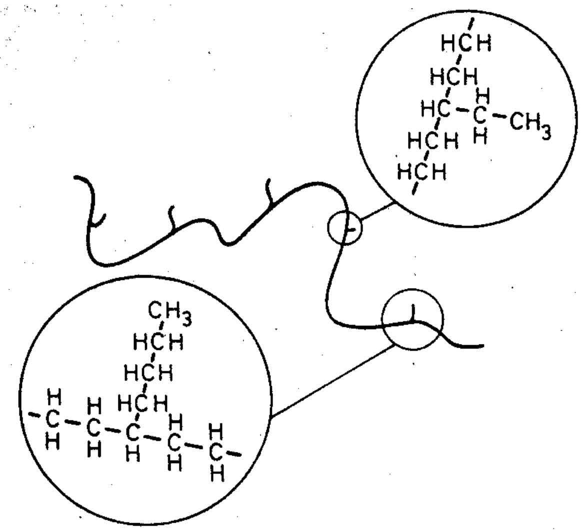


Fig. 1.1. Side branched polyethylene.

Steric – mean square distance of a freely jointed chain

$$\left\langle R^2 \right\rangle_0 = n b_n{}^2 = C_\infty n l^2 = N b^2 = L b_K = N_K b_K{}^2$$

n # of backbone bonds

b_n Length of an effective random work

l Bond length

$C_\infty \equiv \dfrac{b_n^2}{\ell^2}$ Characteristic ratio: 5~10

N Degree of polymerization

b Statistical segment length

L Fully extended length

b_K Kuhn length

$N_K = L / b_K$ # of Kuhn steps

Radius of gyration

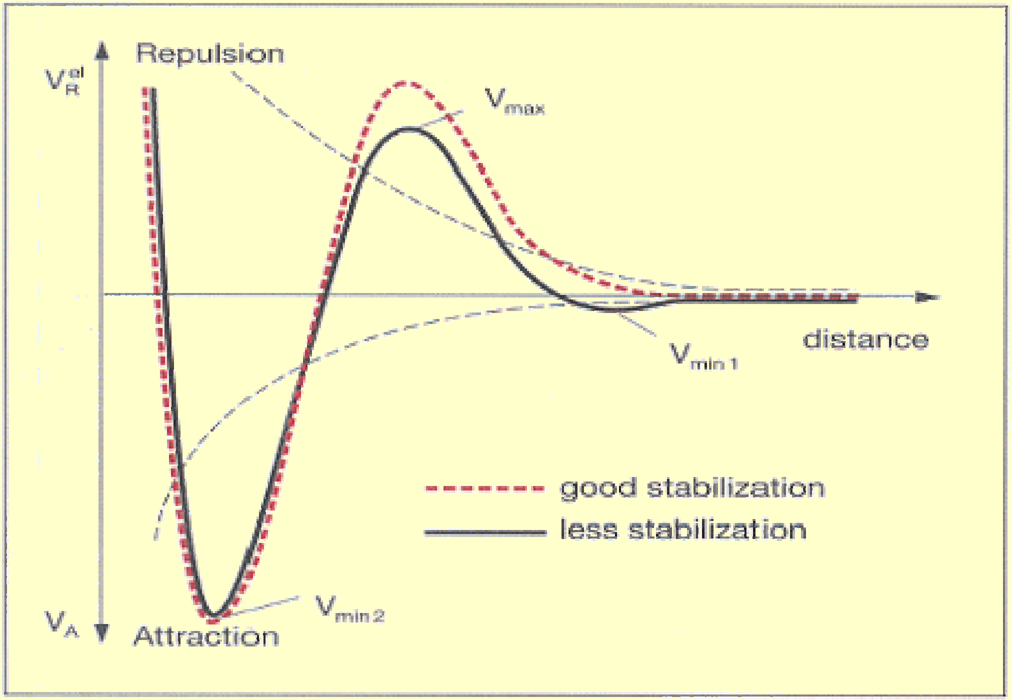
$$R_g = \frac{\left\langle R^2 \right\rangle_0^{1/2}}{\sqrt{6}}$$

van der Waals interactions

due to correlation between the orientation of one dipole and that of its neighbors

Lenard-Jones potential

$$W(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$



the Flory-Huggins model: polymer-polymer mixture

$$\frac{\Delta f}{k_B T} = \frac{\phi_A \ln \phi_A}{\upsilon_A N_A} + \frac{\phi_B \ln \phi_B}{\upsilon_B N_B} + \frac{\chi}{\upsilon}\phi_A \phi_B$$

f=free energy of mixing

most polymer blends are immiscible

$$\chi = \frac{\upsilon_0}{k_B T}(\delta_A - \delta_B)^2$$

for liquid. For polymers, not computed, but adjusted to obtain the best agreement between theory and experimental data

$$\chi = \frac{A}{T} + B$$

UCST, LCST

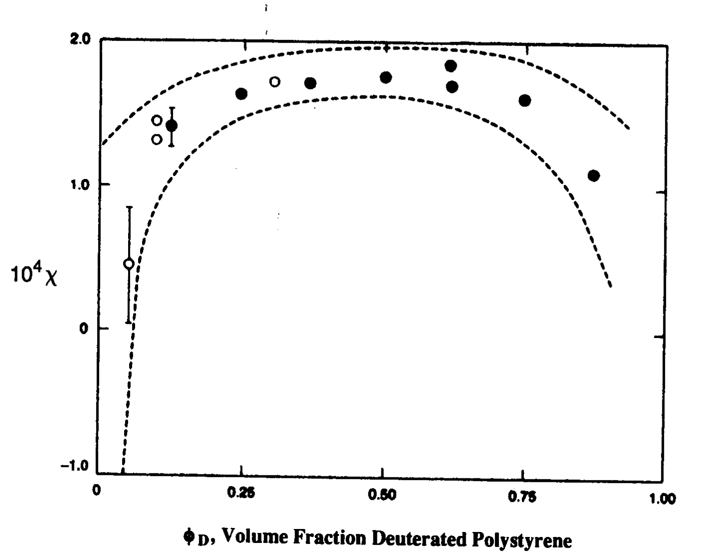


Figure 2.10 χ versus volume fraction of deuterated polystyrene in an isotopic blend of deuterated and hydrogenated polystyrenes at 160°C. The degrees of polymerization are: (●) $N_H = 8700$, $N_D = 11,500$; and (○) $N_H = 15,400$, $N_D = 11,500$. The dashed lines are the error limits. (Reprinted with permission from Londono et al., Macromolecules 27:2864. Copyright 1994, American Chemical Society.)

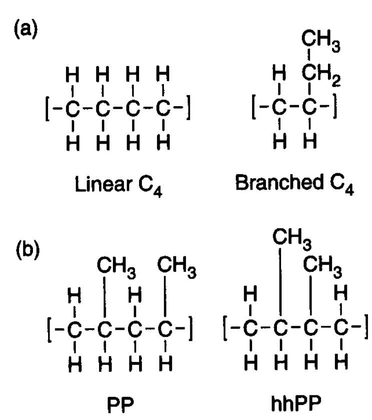


Figure 2.11 **(a)** Linear and ethyl-branched monomers that, when copolymerized together at various ratios, give polymers with a wide range of different ethyl branch content. By mixing together polymers with different levels of ethyl branching and measuring χ by neutron scattering, theories of polymer miscibility can be tested. **(b)** Repeat units for polypropylene and "head-to-head" polypropylene. (Reprinted with permission from Krishnamoorti et al., Macromolecules 27:3073. Copyright 1994, American Chemical Society.)

van der Waals interactions - suspensions

$$W_{vdw}(spheres) = -\frac{A_H}{12}\left\{\frac{1}{(x+1)^2-1}+\frac{1}{(1+x)^2}+2\ln\left[1-\frac{1}{(1+x)^2}\right]\right\}$$

$$W_{vdw}(spheres) \approx \frac{-A_H a}{12D}$$

$$W_{vdw}(flat\, plates) = \frac{-A_H}{12\pi D^2}$$

$$A_H \approx 2.2\times10^{-20}\, J$$ Hamaker constant

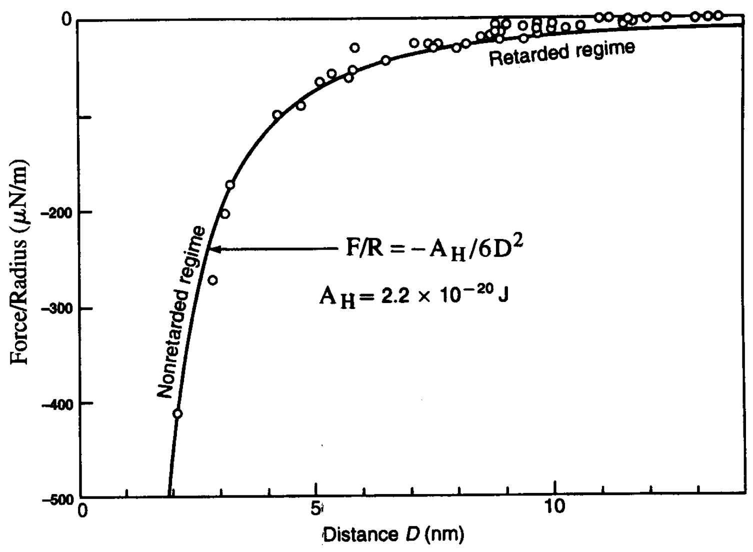


Figure 2.12 Van der Waals force F between two curved mica surfaces of radius $R \approx 1$ cm in water and electrolyte solutions. The line is the fitted van der Waals force with Hamaker constant $A_H = 2.2 \times 10^{-20}$ J. At distances D greater than 5 nm, the force is closer to zero than predicted because of retardation effects. (From Israelachvili and Adams 1978; and Israelachvili 1992, reprinted with permission from Academic Press.)

Electrostatic interactions

The Poisson-Boltzmann equation

Local charge imbalance close to charged surfaces due to mobile ions

Number density is given by the Boltzmann distribution

$$n_i = n_{0i} \exp(-z_i e \psi / k_B T)$$

Electric potential is determined by the Poisson-Boltzmann equation

$$\varepsilon \varepsilon_0 \nabla^2 \psi = -\sum_i z_i e n_{0i} e^{-z_i e \psi / k_B T}$$

For a symmetric electrolyte $\psi(x) = \frac{2k_B T}{ez} \ln\left[\frac{1+\gamma e^{-\kappa x}}{1-\gamma e^{-\kappa x}}\right]$

For a weak surface potential $\psi(x) \approx \frac{4k_B T}{ez} \gamma \exp(-\kappa x) \approx \psi_s \exp(-\kappa x)$

Exponential decay with a decay length of Debye length κ^{-1}