Lecture 16

Entanglement effects \( N \gg N_c \)

Tube or "septation" model

\[ \psi(t) = \sum_\rho \frac{\delta}{\rho^2 \pi} e^{-\rho^2 t/\tau_\rho} \]

Prim. chain

\[ LA = N b^2 = R^2 \]

\[ a = N_c^{1/2} b \]

moves with \( \theta_c = \frac{L \Gamma}{N \nu} \)

\[ I_d = \frac{2 a^2}{D_\nu \pi^2} = \frac{1}{\pi^2} \frac{\gamma N^3 \beta^4}{k_B T a^2} \approx \frac{N^3}{N_c} \]
to move a distance the tube diameter \( \Delta \). This is the time at which the entanglement constraints are first felt.

From the Rouse model:

\[
\langle \left[ \mathbf{r}(s, t_e) - \mathbf{r}(s, 0) \right]^2 \rangle \approx a^2
\]

\[
\Rightarrow \quad t_e \approx a^4 \gamma / (k_b T b^2) \sim N^0 N_0^2
\]

Evidently,

\[
T_e \sim N^0 \ll T_R \sim N^2 \ll T_d \sim N^3
\]

Consider a small step strain.

For \( t \ll t_e \):

\[
G(t) = \rho_e k_b T \left( \frac{t}{a^2} \right)^{-\frac{3}{2}} \quad -T_R^2
\]

\[
\approx \rho_e k_b T \int_0^{T_R^2} \frac{\rho e}{b^2} \quad -T_R^2
\]

\[
\sim \rho_e k_b T \left( \frac{T_R}{a^2} \right)^{1/2}
\]

For \( t \geq t_e \):

\[
G(t) = G_N \left[ 4(t) \right]
\]

"plateau stress relaxes by diffusional creep of deformed tube"
For smooth crossover,

\[ G(t) \approx \frac{G_N^{(0)}}{N_e} \approx \frac{\alpha}{N_e} \frac{k_B T}{N_e} \]

or

\[ G_N^{(0)} = \frac{b^2}{a^2} k_B T \approx \frac{c}{N_e} \frac{k_B T}{N_e} \]

Overall:

\[ G(t) \approx G_N^{(0)} \left( \frac{te}{e} \right)^{-1/2} \]

\[ t \geq \frac{Te}{e} \quad G(t) = G_N^{(0)} \sum_{p_{ad}} \frac{e^{-\frac{e}{p_{ad}}}}{p_{ad}} e^{-p_{ad}t/Te} \]

If we form the complex modulus:

\[ G^{*}(s) = G' + iG'' = i\omega \int_{-i\infty}^{i\infty} e^{-st} G(t) \]

The elastic modulus looks like:
The viscosity turns out to be

$$\eta = G_N \int_0^\infty dt \, \psi(t) = \frac{10}{72} G_N (c) \tau_2 \sim N^3$$

Finally, what does the tube/reptation model predict for the COM diffusion coeff? Consider the time $T_r$ for the tube to be "renewed" by curvilinear diffusion of the BC:

$$\langle s^2 \rangle \sim 2 D_c T_r \sim L^2$$

The COM has been displaced by a
typical chain size $R \sim \sqrt{aL}$ in the time $\tau_R \sim L^2/\ell_0 \sim \ell_0$. Hence,

$$D_0 \sim \frac{R^2}{\tau_R} \sim \frac{aL}{L^2/\ell_0} \sim D_0 \frac{a}{L}$$

$$\sim D_0 \frac{a^2}{b^2N} \sim \frac{k_B T a^2}{\gamma b^2 N^2} \sim \frac{N_0^2}{N^2}$$

In summary, the reptation model suggests

$$\tau \sim N^3, \quad D_0 \sim N^{-2}, \quad \eta \sim N^3$$

Indeed, the prediction $D_0 \sim N^{-2}$ is borne out in experiments! The current experimental situation regarding the predictions for $\tau \sim \eta \sim N^3$ is that indeed this exponent is correct for very large $N$, but that for more modest $N > N_0$, a regime of $\tau \sim \eta \sim N^{3.4}$ exists. This is believed to reflect a combination of contour length fluctuations and constraint release, both operative at more modest molecular weights.
Finally, we can correct our semi-dilute solution results to include entanglement effects. For example

\[ D_0 = \frac{k_B T}{\Pi_s R^2} F(c/c^*) \sim \frac{k_B T}{\Pi_s N^2} (c/c^*)^{\mu} \]

choosing \( \mu \) s.t. \( D_0 \sim N^{-2} \) requires

\[ \mu = -(2-v)/(3v-1) \approx -\frac{3}{4} \]

\[ D_0 \sim N^{-\frac{3}{4}} \]

Similarly,

\[ \eta = \Pi_s \Theta(c/c^*) \sim \Pi_s \left( \frac{N}{c^*} \right)^{\frac{3}{4}(3v-1)} \]

\[ \eta \sim N^{\frac{3}{4}} \]

\[ \Theta \sim \Theta_s H(c/c^*) \sim \Pi_s N^\delta \left( \frac{3}{k_B T} \right)^{\frac{3}{4}(3v-1)} \]

\[ \Theta \sim N^{\frac{3}{4}} \]

\[ C_1^{(c)} = \frac{c}{N} k_B T K(c/c^*) \sim \frac{c}{N} k_B T (c/c^*)^{\frac{1}{4}(3v-1)} \]

\[ C_1^{(c)} \sim N^2 c^{\frac{3}{4}} \]

All these expressions work reasonably well.
In this section of the course, we will turn to discuss the description of time-dependent phenomena associated with phase transformations. For simplicity, we work in the context of a familiar phase transition—liquid/gas transformations. Recall the phase diagram of a 2-component fluid in the $P-T$ plane:

In the $T-P$ plane, $P = \frac{N}{V}$:

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9. Kinetics of Phase Transformations
For $T < T_c$, we can have $L-G$ coexistence over a range of densities. The coexistence curve is obtained by:

\[ T_x = T_\beta \quad \text{thermal equil.} \]
\[ P_x = P_\beta \quad \text{mech. equil.} \]
\[ \mu_x = \mu_\beta \quad \text{chem. equil.} \]

A convenient way to study this curve is in terms of a Helmholtz free energy density, $f(\rho, T)$

\[ A(N, V, T) = V \cdot f(\rho, T) \]

The van der Waals EOS, e.g., gives

\[ f(\rho, T) = k_B T \rho \ln \rho - k_B T \rho a \ln(1 - b \rho) \]

\[ - a \rho^2 \]

The chemical potential is then

\[ \mu = \left. \frac{\partial A}{\partial N} \right|_{V, T} = V \left. \frac{\partial f}{\partial N} \right|_V \left. \frac{\partial f}{\partial \rho} \right|_T \]

\[ \mu = \left. \frac{\partial f}{\partial \rho} \right|_T \]

The pressure is:
\[ P = -\frac{\partial A}{\partial V} \mid_{N,T} = -f - \nu \frac{\partial f}{\partial V} \nu \frac{\partial f}{\partial \rho} \]

or

\[ P = \rho \mu - f \]

Hence, the existence of the binodal curve is obtained from solving

\[ \frac{\partial f}{\partial \rho} \bigg|_{\rho_0} = \frac{\partial f}{\partial \rho} \bigg|_{\rho_0} \]

\[ \rho_0 \frac{\partial f}{\partial \rho} \bigg|_{\rho_0} - f(\rho_0, T) = \rho_0 \frac{\partial f}{\partial \rho} \bigg|_{\rho_0} - f(\rho_0, T) \]

for \( \rho_0, \rho_0 \) at some \( T < T_c \).

A plot of \( f(\rho, T) \) vs \( \rho \) for such a \( T \) looks like:

A mechanically stable system
requires that \( \frac{\partial P}{\partial p} \bigg|_{T} \geq 0 \). But

\[
\frac{\partial P}{\partial p} = \frac{\partial}{\partial p} \left( \rho \mu - f \right) = \rho \frac{\partial^2 f}{\partial p^2}
\]

Thus, the dashed region of \( f \) for

\( \rho_{x} < \rho < \rho_{s} \), where \( \frac{\partial^2 f}{\partial p^2} < 0 \) is unstable. These spinodal densities are obtained as the two roots of

\[
\frac{\partial^2 f}{\partial p^2} = 0
\]

for \( T < T_c \). Thus, we have:

![Spinodal curve and binodal diagram]

We can now ask about the fate of an initially homogeneous, one-phase fluid whose temperature is lowered rapidly.
according to path 1 or path 2.

Path 1: The fluid has a T, P between the binodal and spinodal curves. It is locally stable against small density perturbations, but globally unstable against phase separation. We say the fluid is metastable. There is a free energy barrier to surmount and the new phases will develop by a nucleation and growth process.

Path 2: The fluid has a T, P inside the spinodal. It is locally unstable to small density perturbations and will spontaneously begin to phase separate with no energy barrier. This process is known as spinodal decomposition.

A. Field Theory Models
B. To analyze both N&G and 3D processes, we need a theory capable of describing the energetics of inhomogeneous fluids. In general, this is the domain of density functional theory. For our purposes, however, we will use a very simple free energy