Lecture 3: Example Systems

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$$Z = \frac{1}{n! \lambda_T^{3n}} \int d\underline{r}^n \, e^{-\beta U}$$

$$= \frac{V^n Z_0}{n!} \int \mathcal{D}w \, e^{-\mathcal{H}[w]}$$

$$\mathcal{H} = \int d\underline{r} \int d\underline{r}' \, w(\underline{r}) \, u^{-1}(\underline{r}, \underline{r}') \, w(\underline{r}')$$

$$- n \log Q[iw]$$

Two-Component system:

$$n_T = n_A + n_B \qquad \rho_0 = \frac{n_T}{V}$$

$$\phi_A = \frac{n_A}{V} \qquad \phi_B = \frac{n_B}{V}$$

$$\hat{\rho}_A(\underline{r}) = \sum_{j=1}^{n_A} \delta(\underline{r} - \underline{r}_j) \qquad \hat{\rho}_B(\underline{r}) = \sum_{j=1}^{n_B} \delta(\underline{r} - \underline{r}_j)$$

$$\hat{\rho}_+(\underline{r}) = \hat{\rho}_A(\underline{r}) + \hat{\rho}_B(\underline{r})$$

$$u(\underline{r}_{ij}) = kT \cdot \chi \cdot \delta(\underline{r}_i - \underline{r}_j)$$

Assume - $\chi > 0$
- Incompressible system

$$\beta U = \chi \int d\underline{r} \int d\underline{r}' \, \hat{\rho}_A(\underline{r}) \, \delta(\underline{r}-\underline{r}') \, \hat{\rho}_B(\underline{r}')$$

$$Z = \frac{z_0^{\,n}}{n_A! \, n_B!} \int d\underline{r}^{n_T} \left\{ e^{-\chi \int dr \int dr' \hat{\rho}_A(r) \delta(r-r') \hat{\rho}_B(r')} \cdot \delta\left[\hat{\rho}_+(\underline{r}) - \rho_0\right] \right\}$$

Introduce $\hat{\rho}_-(\underline{r}) = \hat{\rho}_A(\underline{r}) - \hat{\rho}_B(\underline{r})$

$$\hat{\rho}_A(\underline{r}) = \frac{1}{2}\left(\hat{\rho}_+(\underline{r}) + \hat{\rho}_-(\underline{r})\right)$$

$$\hat{\rho}_B(\underline{r}) = \frac{1}{2}\left(\hat{\rho}_+(\underline{r}) - \hat{\rho}_-(\underline{r})\right)$$

Plug into βU:

$$\hat{\rho}_A(\underline{r}) \cdot \hat{\rho}_B(\underline{r}') = \frac{1}{2}\left(\hat{\rho}_+(\underline{r}) + \hat{\rho}_-(\underline{r})\right) \cdot \frac{1}{2}\left(\hat{\rho}_+(\underline{r}') - \hat{\rho}_-(\underline{r}')\right)$$

$$= \frac{1}{4}\left(\hat{\rho}_+(\underline{r})\hat{\rho}_+(\underline{r}') - \hat{\rho}_-(\underline{r}) \cdot \hat{\rho}_-(\underline{r}')\right)$$

$$\frac{\chi}{4} \int dr \int dr' \left[\hat{\rho}_+(\underline{r}) \cdot \delta(r-r') \, \hat{\rho}_+(r') - \hat{\rho}_-(\underline{r}) \, \delta(r-r') \, \hat{\rho}_-(r') \right]$$

$\hookrightarrow \rho_0$ $\hookrightarrow \rho_0$

$$\exp(-\beta U) = \exp\left(\frac{\chi}{4} \rho_0^2 \cdot V\right) \exp\left(\frac{\chi}{4} \int dr \int dr' \, \hat{\rho}_-(r) \, \delta(r-r') \, \hat{\rho}_-(r')\right)$$

$$\exp(-\beta U) = \exp\left(\frac{\chi}{4}\rho_0^2 \cdot V\right) \exp\left(\frac{\chi}{4}\int dr \int dr' \hat{\rho}_-(r)\, \delta(r-r')\, \hat{\rho}_-(r')\right)$$

Second exponential a field conjugate to $\hat{\rho}_-$:

$$\exp\left(\frac{\chi}{4}\int dr \int dr' \hat{\rho}_-(r)\, \delta(r-r')\, \hat{\rho}_-(r')\right)$$

$$= \frac{1}{\Omega_0}\int \mathcal{D}\omega_- \exp\left(-\frac{1}{\chi}\int dr [\omega_-(r)]^2 + \int dr\, \omega_-(r)\, \hat{\rho}_-(r)\right)$$

$$\delta[\hat{\rho}_+ - \rho_0] = \int \mathcal{D}\omega_+\, e^{i\int dr\, \omega_+(r)[\hat{\rho}_+(r) - \rho_0]}$$

Plug into Z:

$$Z = \frac{Z_1}{n_A!\, n_B!} \int \mathcal{D}\omega_+ \int \mathcal{D}\omega_- \Big\{ \exp\left(-\frac{1}{\chi}\int dr\, \omega_-^2(r) - i\rho_0 \int dr\, \omega_+(r)\right)$$

$$\int dr^{n_A} \exp\Big(-\int dr\, \hat{\rho}_A(r)\, \overbrace{[i\omega_+(r) + \omega_-(r)]}^{=\mu_A(r)}\Big)$$

$$\int dr^{n_B} \exp\Big(-\int dr\, \hat{\rho}_B(r)\, \underbrace{[i\omega_+(r) - \omega_-(r)]}_{=\mu_B}\Big)\Big\}$$

$$= \frac{Z_1 V^{n_A+n_B}}{n_A!\, n_B!} \int \mathcal{D}\omega_- \int \mathcal{D}\omega_+\, e^{-\mathcal{H}[\omega_-, \omega_+]}$$

$$\mathcal{H}[\omega_-, \omega_+] = \int dr \left[\frac{1}{\chi}\omega_-^2(r) - i\rho_0\, \omega_+(r)\right]$$

$$-n_A \log Q_A[i\omega_+ + \omega_-]$$

$$-n_B \log Q_B[i\omega_+ - \omega_-]$$

$$Q_A = \frac{1}{V}\int dr\; e^{-(i\omega_+ + \omega_-)}$$

$$Q_B = \frac{1}{V}\int dr\; e^{-(i\omega_+ - \omega_-)}$$

Mean-field Approximation

$$Z = \frac{z_1 V^{n_T}}{n_A!\, n_B!}\int D\omega_+ \int D\omega_-\; e^{-\mathcal{H}} = e^{-\beta F}$$

$$\approx \frac{z_1 V^{n_T}}{n_A!\, n_B!}\; e^{-\mathcal{H}[\omega_+^*, \omega_-^*]} = e^{-\beta F}$$

$\omega_+^*(r)$, $\omega_-^*(r)$ are field configs that minimize F

$$\frac{\delta \mathcal{H}}{\delta \omega_+(r)} = 0 \qquad \frac{\delta \mathcal{H}}{\delta \omega_-(r)} = 0$$

Homogeneous MFA $\omega_+(r) = \omega_+$

$$\beta F = \mathcal{H} - n_A \log V - n_B \log V + n_A \log n_A$$

$$+ n_B \log n_B - n_A - n_B + F_0$$

$$\mathcal{H} = \frac{1}{2\chi}\omega_-^2 \int dr \;\;\; - i\rho\omega_+ \int dr$$

$$\mathcal{H} = \frac{1}{\chi} w_- \int dr(\;) - i \rho_0 w_+ \int dr(\;)$$

$$- n_A \log Q_A - n_B \log Q_B$$

$$Q_A = \frac{1}{V} \cdot e^{-iw_+ + w_-} \cdot \int dr(\;)$$

$$= e^{-iw_+ + w_-}$$

$$Q_B = e^{-iw_+ - w_-}$$

Plug into $\mathcal{H}$

$$\mathcal{H} = \frac{V}{\chi} w_-^2 - i \frac{n_A + n_B}{V} \cdot w_+ V$$

$$- n_A(-iw_+ + w_-) - n_B(-iw_+ - w_-)$$

w_+ drops out!

$$\frac{F}{VkT} = \frac{1}{\chi} w_-^2 - \phi_A w_- + \phi_B w_-$$

$$+ \phi_A \log \phi_A + \phi_B \log \phi_B - f_0$$

$$\frac{\partial (F/V)}{\partial w_-} = 0 = \frac{2 w_-^*}{\chi} - \phi_A + \phi_B$$

$$w_-^* = \frac{\chi}{2}(\phi_A - \phi_B)$$

Plug in, simplify:

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$$\frac{F}{VkT} = \frac{\chi}{2}\phi_B\phi_A + \phi_A\log\phi_A + \phi_B\log\phi_B - f_0$$

Derive Poisson-Boltzmann

$$\hat{\rho}_c = Z_+\sum_{j=1}^{n_+}\delta(r-r_j) - Z_-\sum_{j=1}^{n_-}\delta(r-r_j)$$

$n = n_+ + n_-$ total particles

$n_+ \cdot Z_+ - n_- \cdot Z_- = 0$ by electroneutrality

Interactions through Coulomb's law:

$$u(r,r') = kT\frac{l_B}{|r-r'|}, \quad l_B = \text{"Bjerrum length"} = \frac{e^2}{kT\varepsilon_0\varepsilon_r}$$

$$u^{-1}(r,r') = \frac{-1}{4\pi l_B}\nabla^2\delta(r-r')$$

$$u^{-1}(k) = \frac{(2\pi)^3}{l_B}k^2$$

$$\beta U = \frac{1}{2}\int dr\int dr'\,\hat{\rho}_c(r)\frac{l_B}{|r-r'|}\hat{\rho}_c(r')$$

$$Z = \frac{z_0'}{n_+!n_-!}\int d\underline{r}^n \exp(-\beta U)$$

$$= \frac{z_0}{n_+!n_-!}\int D\psi \int d\underline{r}^n \exp\left[-\frac{1}{2}\int dr\int dr'\, \psi(r)\left[\frac{-1}{4\pi l_B}\nabla^2\delta(r-r')\right]\psi(r') - i\int dr\, \psi(r)\,\hat{\rho}_c(r)\right]$$

Focus on the term w/ particle coords:

$$\int d\underline{r}^n e^{-i\int dr\, \psi(r)\hat{\rho}_c(r)}$$

$$= \int dr^{n_+} e^{-i\int dr\, \psi(r)\cdot\sum_{j=1}^{n_+}\delta(r-r_j)\cdot z_+}$$

$$\times \int dr^{n_-} e^{+i\int dr\, \psi(r)\sum_j^{n_-}\delta(r-r_j)\cdot z_-}$$

$$= (V\,Q[i z_+\psi])^{n_+}\cdot(V\,Q[-i z_-\psi])^{n_-}$$

$$Z = \frac{z_1 V^n}{n_+!n_-!}\int D\psi\, e^{-\mathcal{H}[\psi]}$$

$$\mathcal{H}[\psi] = -\frac{1}{2}\int dr\, \psi(r)\frac{1}{4\pi l_B}\nabla^2\psi(r)$$

$$- n_+\log Q[i z_+\psi] - n_-\log Q[-i z_-\psi]$$

First term often re-written:

$$\int dr\, \psi(r)\, \nabla^2 \psi(r) = \int dr\, \psi(r)\, \nabla \cdot \nabla \psi \quad \text{I.B.P.}$$

$$= \underbrace{\oint d\ell\, (\ )}_{0} - \int dr\, \underline{\nabla}\psi \cdot \underline{\nabla}\psi$$

$$= \quad - \int dr\, |\underline{\nabla}\psi|^2$$

$$\mathcal{H}[\psi] = \frac{1}{8\pi l_B} \int dr\, |\nabla\psi|^2 - n_+ \log Q_+ - n_- \log Q_-$$

$$Z = \frac{z_1 V^n}{n_+!\, n_-!} \int \mathcal{D}\psi\, e^{-\mathcal{H}} \approx \frac{z_1 V^n}{n_+!\, n_-!}\, e^{-\mathcal{H}[\psi^*]}$$

$$\left(\frac{\delta \mathcal{H}}{\delta \psi}\right|_{\psi^*} = 0 = \frac{1}{8\pi l_B} \underbrace{\frac{\delta}{\delta\psi} \int dr\, |\nabla\psi|^2}_{= -2\nabla^2\psi(r)}$$

$$+ i z_+ \tilde{\rho}_+(r) - i z_- \tilde{\rho}_-(r)$$

$$\tilde{\rho}_\pm(r) = \frac{1}{VQ}\, e^{\mp i z_\pm \psi(r)}$$

$$-\frac{1}{4\pi l_B} \nabla^2 \psi(r) + i \tilde{\rho}_c(r) = 0$$

$$\nabla^2 \psi(r) = 4\pi l_B\, i\, \tilde{\rho}_c(r)$$

$$\nabla^2 (i\psi(r)) = -4\pi l_B\, \tilde{\rho}_c(r)$$

Interpret $i \cdot \Psi(r)$ as the electrostatic potential, consistent w/ Poisson-Boltzmann equation

Maier-Saupe Fluid

Ad-lib quick overview of LCs:
- anisotropic molecules, can undergo an isotropic to nematic transition
- can occur upon changes in concentration of larger objects in solution (lyotropic)
- or upon changes in T for molecular liquid crystals (thermotropic)
- We'll consider a simple model of the latter case

Important new piece of information we need: each molecule now carries a unit orientation, $\mathbf{u}_i$

$\mathbf{u}_i$ a unit vector oriented along the mesogen

This new degree of freedom shows up in our molecular partition function, and interaction potential will depend on mutual orientation of the molecules

$$\mathcal{Z} \;=\; z_1 \int d\mathbf{r}^n \int d\mathbf{u}^n \; e^{-\beta U(\mathbf{r}^n,\mathbf{u}^n)} \tag{1}$$

The total densities are now written as:

$$\hat{\rho}(\mathbf{r},\mathbf{u}) = \sum_i^n \delta(\mathbf{r}-\mathbf{r}_i)\,\delta(\mathbf{u}-\mathbf{u}_i) \tag{2}$$

$$\beta U = \frac{1}{2}\int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{u}\, d\mathbf{u}'\, \hat{\rho}(\mathbf{r},\mathbf{u}) v(\mathbf{r},\mathbf{r}',\mathbf{u},\mathbf{u}')\hat{\rho}(\mathbf{r}',\mathbf{u}')$$

Pair potential for the MS model is typically written as

$$v(\mathbf{r},\mathbf{r}',\mathbf{u},\mathbf{u}') = -u_0\,\delta(\mathbf{r}-\mathbf{r}')\, P_2(\mathbf{u}\cdot\mathbf{u}') \tag{3}$$

$$P_2(x) = \frac{1}{2}(3x^2-1) \tag{4}$$

Sketch $P_2(x)$, talk through the potential a bit: $u_0 > 0$ favors alignment, competing with entropy of disorder

This form not compatible with Hubbard-Stratonovich transformation because it's not Gaussian

We'll use a different form. I first saw it in a paper by Pryamitsyn and Ganesan, 2004 JCP, where instead of writing the potential using P_2, we write a tensor form:

$$\beta U = -\frac{\mu}{2\rho_0}\int d\mathbf{r}\, \hat{\mathbf{S}}(\mathbf{r}) : \hat{\mathbf{S}}(\mathbf{r}) \tag{5}$$

$$\hat{\mathbf{S}}(\mathbf{r}) = \sum_i \delta(\mathbf{r}-r_i)\,[\mathbf{u}_i\mathbf{u}_i - \frac{1}{3}\mathbf{I}] \tag{6}$$

This is a form we can work with

Write our total partition function, now with an included incompressibility constraint:

$$\mathcal{Z} = z_1 \int d\mathbf{r}^n \int d\mathbf{u}^n\, \delta\left[\rho_0 - \hat{\rho}(\mathbf{r})\right] \exp\left[\frac{\mu}{2\rho_0}\int d\mathbf{r}\, \hat{\mathbf{S}}(\mathbf{r}) : \hat{\mathbf{S}}(\mathbf{r})\right]$$

Delta function behaves just like regular solution theory above

Orientation term uses the positive Gaussian form, and we introduce a *tensor field* $\mathbf{M}(\mathbf{r})$

$$\begin{aligned}\mathcal{Z} &= z_2 \int \mathcal{D}w_+ \int \mathcal{D}\mathbf{M}\; e^{-\mathcal{H}[w_+,\mathbf{M}]} &(7)\\ \mathcal{H} &= \frac{\rho_0}{2\mu} \int d\mathbf{r}\; \mathbf{M}(\mathbf{r}) : \mathbf{M}(\mathbf{r}') - i\rho_0 \int d\mathbf{r} w_+(\mathbf{r}) &(8)\\ &-n \log Q[iw_+, \mathbf{M}]\end{aligned}$$

The molecular partition function takes the form:

$$Q = \frac{1}{4\pi V} \int d\mathbf{r} \int d\mathbf{u}\; \exp\left[-iw_+(\mathbf{r}) + \mathbf{M}(\mathbf{r}) : [\mathbf{uu} - \frac{1}{3}\mathbf{I}]\right]$$

Define the argument of the exponential as $\mu_{LC}(\mathbf{r}, \mathbf{u})$, the potential field for the LC mesogen at position r and orientation u

Two interesting operators for this theory, first the total density:

$$\begin{aligned}\tilde{\rho}(\mathbf{r}) &= -\frac{\delta}{\delta iw_+(\mathbf{r})} (n \log Q) &(9)\\ &= \frac{n}{4\pi VQ} \int d\mathbf{u}\; e^{-\mu_{LC}(\mathbf{r},\mathbf{u})} &(10)\end{aligned}$$

and a local orientation tensor

$$\tilde{\mathbf{S}}(\mathbf{r}) = \frac{n}{4\pi VQ} \int d\mathbf{u}\; [\mathbf{uu} - \frac{1}{3}\mathbf{I}]\; e^{-\mu_{LC}(\mathbf{r},\mathbf{u})} \qquad (11)$$

This operator tells you about the orientation distribution of all the molecules at $\mathbf{r}$

If everything is aligned, then the integral is dominated by a single orientation $\mathbf{u}$

Now, since we have two fields in our equation, we can invoke a mean-field approximation on both:

$$\frac{\delta \mathcal{H}}{\delta w_+(r)} = 0 \tag{12}$$

$$= -i\rho_0 + i\tilde{\rho}(\mathbf{r}) \tag{13}$$

This gives the trivial result that the total density is ρ_0 everywhere

And from the M-field:

$$\frac{\delta \mathcal{H}}{\delta \mathbf{M}(\mathbf{r})} = 0 \tag{14}$$

$$= \frac{\rho_0}{2\mu}\mathbf{M}(\mathbf{r}) - \tilde{\mathbf{S}}(\mathbf{r}) \tag{15}$$

In the end you have to solve for the orientation distribution that solves the pair of equations

Still have the integral over $\mathbf{u}$ that complicates solving it analytically

Can easily be done numerically, probably also analytically, I just don't know the easiest path to the solution

$w_+(r)$ field acts as a Lagrange multiplier enforcing the total density to be ρ_0

μ is a parameter that governs the strength of the potential

For $\mu > \mu_c$, an isotropic-to-nematic transition is predicted