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Cell Model Theory of Polymer Solutions

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ABSTRACT: A statistical thermodynamic theory of a polymer solution is formulated which takes into account concentration inhomogeneities on size scales equal to or larger than the average size of a polymer chain. A generalized cell model is used as the basis for the new polymer solution theory. Closed-form, parametric equations are obtained for solvent and polymer chemical potentials which only reduce to classical (Flory–Huggins) potentials when concentration homogeneity is assumed. In a good solvent, the calculated second virial coefficient decreases with molecular weight ($M^{-1/5}$ dependence), in good agreement with available experimental data. In dilute solutions, chain dimensions can be analytically determined; the well-known Flory excluded-volume equation is obtained. Given that D_0 is the infinite-dilution value of the concentration derivative of the chain expansion factor α^2 and C^* is the overlap concentration as defined in scaling theories, it is shown that D_0C^* is a negative constant independent of molecular weight. Although the theory works well in the dilute regime, it begins to break down in the semidilute regime because concentration inhomogeneities smaller than the average chain size are ignored.

I. Introduction

A crucial assumption of Flory–Huggins (FH) theory[1,2] is that it assumes that a polymer solution is uniform in monomer concentration. However, concentration inhomogeneities exist in a polymer solution that are related to the intrinsic connectivity of the monomers that comprise a polymer chain. In dilute solutions the nonuniform distribution of monomers is extreme; it is here that the inadequacy of FH theory is most transparent. For example, it predicts that the osmotic pressure second virial coefficient (A_2) is independent of molecular weight, whereas it is known to decrease with molecular weight. The assumption of concentration uniformity results in an overestimation of A_2 that is tantamount to overestimating the effects of excluded volume. A more thorough critique of FH theory has recently been given by de Gennes.[3]

There have been a number of attempts by previous investigators to bridge the thermodynamic gap between dilute and concentrated polymer solutions. These studies have usually focused on obtaining either the correct form of the free energy or the concentration dependence of chain dimensions. Examples of the former include the two-phase bridging theory of Koningsveld, Stockmayer, Kennedy, and Kleintjens[4] and its recent refinement by Irvine and Gordon,[5] the Lagrangian field theory of des Cloizeaux,[6] and the self-consistent field theory of Edwards,[7] who introduced the important concept of "screening" of excluded-volume effects. Examples of theories that focus on chain dimensions include the application and extension of des Cloizeaux's ideas by Daoud et al.,[8,9] by de Gennes,[3] and by Moore and Al-Noaimi.[10] These latter theories are commonly referred to as scaling theories and are only applicable in the so-called semidilute regime. Edwards[11,12] has also developed a self-consistent field theory of chain dimensions for semidilute solutions. Historically, one of the earliest attempts was a very ambitious one by Fixman[13] and Fixman and Peterson.[14] They attempted to obtain both the free energy *and* chain dimension behavior *in a unified theory* by using concentration-dependent interaction potentials and radial distribution functions.

In the present paper a statistical thermodynamic theory of a polymer/solvent system is formulated which differs substantially from any previous theory. This new theory is based on a generalized cell model which is outlined in Appendix A. Two special cases of this model correspond to treating the configurational space statistical mechanics of fermions and bosons. In general this model describes particles that follow a distribution law intermediate to Fermi–Dirac and Bose–Einstein distributions.

In applying this model to a polymer/solvent solution, a polymer chain is treated as a uniform-density sphere of "mers". The solution volume is divided into ω cells, each just large enough to accommodate a random-coil polymer chain. For a uniform-density sphere model, the magnitude of the intermolecular interaction is proportional to the overlap volume or covolume. In Appendix B an important theorem is proven that shows for covolume interaction, the process of system "cellularization" leaves the system's interaction energy invariant. Thus, the statistical mechanics of a polymer solution can be usefully approximated by an appropriately modified version of the generalized cell model. Two modifications are required: First, each cell is weighted by a Boltzmann factor involving a FH-type free energy *rather than a simple potential interaction energy*. In the second modification, an elastic entropic contribution is added to the solution's free energy to take into account solvent swelling of the polymer chains.

A condition of equilibrium can be used to calculate the average size (radius of gyration) of the polymer chains. In dilute solutions, this condition can be used to calculate chain dimensions analytically. It is shown that the well-known Flory excluded-volume equation[15] is obtained in the dilute-solution limit. Even in the dilute regime, where polymer molecules are on the average widely separated, chain dimensions decrease with concentration.

Although the theory works well in the dilute regime and in very concentrated solutions, it fails in the intermediate concentration range. An explanation of this failure is given in section III.

II. Cell Model Description of Polymer Solutions

A. Polymer–Polymer Interactions. If a polymer chain containing r "mers" has a radius of gyration S, then the simplest model of such a chain is a sphere of radius proportional to S and with the r mers uniformly distributed throughout the sphere. This model is often referred to as the uniform-density sphere model[16] and was first introduced by Flory.[17] For this type of model, the number of intermolecular mer–mer interactions between two chains will be proportional to the overlap volume or covolume.

The rationale for using a cell model (see Appendix A) to describe the statistical mechanics of a system of interacting polymer chains is expressed in the following

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theorem which is proved in Appendix B.

Theorem. Consider a system of N spherical particles of diameter d whose potential energy is pairwise additive. The system is divided into ω cells each of volume $(\pi/6)d^3$. A system configuration in which all N sphere centers are at cell centers is defined as a cellular configuration. Any system configuration can be converted to a cellular configuration by translating all spheres which are located at off-center positions to the centers of their respective cells. If the pair potential between two spheres is proportional to their covolume, then the process of translating the N spheres to their respective cell centers does not alter the mean value of the system's covolume.

Therefore, if the mean potential energy of the system is proportional to the system covolume, then it remains invariant under the translation. It is this isomorphic property that makes the generalized cell model so useful for treating interacting polymer chains.

Although the proof of the above covolume theorem given in Appendix A is nontrivial, its validity is suggestive on intuitive grounds. Consider the example of noninteracting spheres randomly distributed in space. Now for a given configuration translate the spheres to their respective cell centers. When the spheres are translated some spheres which overlapped with other spheres in the random configuration may now be in cells that are singly occupied (no overlap). Other spheres which did not overlap with any others in the random configuration may now be in multiply-occupied cells. Translation creates and destroys covolume, but the effects tend to cancel. When an average is taken over all possible system configurations, no net change occurs in the average system covolume.

B. Partition Function. Consider a system of N_2 r-mers and N_1 monomer solvent molecules filling an incompressible lattice of $N_T = N_1 + rN_2$ sites. The r-mer chains have a mean-square radius of gyration of $\langle S^2 \rangle$ or an expansion factor α^2 defined by

$$\alpha^2 \equiv \langle S^2 \rangle / \langle S^2 \rangle_0 \tag{1}$$

where $\langle S^2 \rangle_0$ is the mean-square radius of gyration of the chains in *undiluted* polymer ($N_1 = 0$). From this point forward the system is treated as if it contained N_2 identical chains all with the same expansion factor α^2; α is defined with respect to undiluted polymer because it becomes a reference state in what follows. We also assume that $\langle S^2 \rangle_0 \sim r$.

The volume fraction of space, ϕ_α, occupied by a chain is proportional to $r\sigma^3 / \langle S^2 \rangle^{3/2}$, where σ^3 is the volume of a mer or lattice site. Thus

$$\phi_\alpha \sim \frac{r\sigma^3}{\alpha^3 \langle S^2 \rangle_0{}^{3/2}} \sim r^{-1/2}\alpha^{-3} \leq 1 \tag{2}$$

The volume of the chain is proportional to $\langle S^2 \rangle^{3/2} \sim r^{3/2}\alpha^3 \sim r/\phi_\alpha$. Dividing the system into ω cells, we have

$$\omega = N_T/(r/\phi_\alpha) = N_2(\phi_\alpha/\phi_2) \tag{3}$$

where ϕ_2 is the overall polymer volume fraction

$$\phi_2 \equiv rN_2/N_T = 1 - \phi_1 \tag{4}$$

The average number of chains/cell is

$$\lambda \equiv N_2/\omega = \phi_2/\phi_\alpha \tag{5}$$

If the N_2 chains are translated to their respective cell centers, then the appropriate partition function for the cellurized system, relative to pure solvent and polymer, is (see Appendix A)

$$Z = z_{\text{el}}{}^{N_2} Z_c \tag{6}$$

where

$$Z_c = \frac{\omega!}{\prod_{n=0}^{m} \bar{\omega}_n!} \exp[-\beta \sum_{n=0}^{m} \bar{\omega}_n \Delta A_n] \tag{7}$$

$$\ln z_{\text{el}} = \ln \alpha^3 - {}^3\!/_2(\alpha^2 - 1) \tag{8}$$

In applying the cell model to a polymer solution we have made two important modifications to the partition function. First, each cell is weighted by a Boltzmann factor involving a free energy rather than a simple energy. The free energy ΔA_n of a cell containing n chains relative to pure polymer and solvent is assumed to be given by a Flory–Huggins free energy[1]

$$\beta \Delta A_n = rm\left[(1 - n\phi_\alpha) \ln (1 - n\phi_\alpha) + \frac{n\phi_\alpha}{r} \ln (n\phi_\alpha) + n\phi_\alpha(1 - n\phi_\alpha)\chi\right] \tag{9}$$

where $m = 1/\phi_\alpha$ is the maximum number of polymer chains allowed per cell and χ is the usual interaction parameter. The total number of lattice sites/cell equals $rm \equiv r/\phi_\alpha$. The first two terms in brackets in eq 9 are associated with the excluded-volume interaction between the n chains while the χ term takes care of attractive mer–mer, mer–solvent, and solvent–solvent interactions. Notice that $\Delta A_0 = \Delta A_m = 0$. The second modification that we have made is to take into account the change in entropy/chain associated with chain expansion. For this we use the usual Flory expression,[1] $k \ln z_{\text{el}}$, for the elastic entropy.

Equations A6, A7, and A8 that define P_n, Ω, and λ are still applicable here except that E_n is replaced by ΔA_n. Notice that the average volume fraction of polymer/cell is given by

$$\langle n\phi_\alpha \rangle = \langle n \rangle \phi_\alpha = \lambda\phi_\alpha = \phi_2 \tag{10}$$

as it should.

C. Chemical Potentials. With the aid of eq A6, the partition function, eq 6, can be rewritten in a more compact form:

$$Z = e^{-\beta \Delta A} = [(z_{\text{el}}/z)\Omega^{1/\lambda}]^{N_2} \tag{11}$$

where ΔA is the total Helmholtz free energy of the polymer solution relative to pure solvent and polymer. For an incompressible solution

$$\Delta A = N_1 \Delta\mu_1 + N_2 \Delta\mu_2 \tag{12}$$

where $\Delta\mu_1$ and $\Delta\mu_2$ are the relative chemical potentials of solvent and polymer, respectively.

From eq 11 the free energy/lattice site, Δa, is given by

$$\beta \Delta a \equiv \beta \Delta A / N_T = \frac{\phi_2}{r}\left[\ln (z/z_{\text{el}}) - \frac{\ln \Omega}{\lambda}\right] \tag{13}$$

It is now easy to show from the thermodynamic definitions of the chemical potentials that

$$\Delta\mu_1 = \Delta a + \phi_2 \frac{\mathrm{d}\Delta a}{\mathrm{d}\phi_1} \tag{14}$$

and

$$\Delta\mu_2 = r\left[\Delta a + \phi_1 \frac{\mathrm{d}\Delta a}{\mathrm{d}\phi_2}\right] \tag{15}$$

Thus

$$\Delta\mu_2/r - \Delta\mu_1 = \mathrm{d}\Delta a/\mathrm{d}\phi_2 \tag{16}$$

Now Δa is explicitly a function of ϕ_2 and an implicit function of ϕ_2 through α^2; so

$$\frac{d\Delta a}{d\phi_2} = \left.\frac{\partial \Delta a}{\partial \phi_2}\right|_{\alpha^2} + \left.\frac{\partial \Delta a}{\partial \alpha^2}\right|_{\phi_2}\frac{d\alpha^2}{d\phi_2} \tag{17}$$

However, the condition of equilibrium is defined as

$$\left.\frac{\partial \Delta a}{\partial \alpha^2}\right|_{\phi_2} = 0 \tag{18a}$$

Using eq A6, A7, and 13, we can rewrite 18a as

$$\left[\ln \Omega - \beta\phi_\alpha\left\langle\frac{\partial \Delta A_n}{\partial \phi_\alpha}\right\rangle\right]\frac{\partial \phi_\alpha}{\partial \alpha} + \phi_2\frac{\partial \ln z_{\mathrm{el}}}{\partial \alpha} = 0 \tag{18b}$$

Equation 18 is the "equation of state" for the chains; it relates chain size to polymer concentration and temperature.

Combining eq 13, 17, and 18a, we obtain

$$\beta\frac{d\Delta a}{d\phi_2} = \frac{1}{r}\left[\ln(z/z_{\mathrm{el}}) + \phi_2\left.\frac{\partial \ln z}{\partial \phi_2}\right|_{\alpha_2} - \phi_\alpha\left.\frac{\partial \ln \Omega}{\partial \phi_2}\right|_{\alpha^2}\right] \tag{19a}$$

Now from eq A7, we have

$$\left.\frac{\partial \ln \Omega}{\partial \phi_2}\right|_{\alpha^2} = \lambda\left.\frac{\partial \ln z}{\partial \phi_2}\right|_{\alpha^2} \tag{20}$$

and thus eq 19a becomes

$$\beta\frac{d\Delta a}{d\phi_2} = \frac{1}{r}\ln(z/z_{\mathrm{el}}) \tag{19b}$$

Substituting eq 19b and 13 into (14) yields the chemical potential of the solvent

$$\beta\Delta\mu_1 = -\frac{\phi_2}{r}\frac{\ln \Omega}{\lambda} \tag{21}$$

Similarly, from eq 15 we obtain the chemical potential of the polymer

$$\beta\Delta\mu_2 = \ln(z/z_{\mathrm{el}}) - \phi_2\frac{\ln \Omega}{\lambda} \tag{22}$$

A zeroth-order approximation to the chemical potentials can be obtained by approximating Ω by its maximum term; i.e.

$$\Omega \simeq z^{n^*}e^{-\beta\Delta A_{n^*}} \tag{23a}$$

where n^* is defined by the equation

$$\ln z - \beta\frac{\partial \Delta A_n}{\partial n} = 0 \tag{24}$$

In other words, n is treated as a continuous variable and eq 24 defines that value of n which yields the maximum term. However, eq A8 requires that

$$n^* \equiv \langle n\rangle \equiv \lambda \tag{25}$$

Equations 24 and 25 taken together require that

$$\ln z = \beta\left.\frac{\partial \Delta A_n}{\partial n}\right|_{n=\lambda} \tag{26}$$

Substituting eq 26 into (23a) yields

$$\ln \Omega \simeq \beta\left[\lambda\left.\frac{\partial \Delta A_n}{\partial n}\right|_{n=\lambda} - \Delta A_{n=\lambda}\right] \tag{23b}$$

Substituting eq 23b into (21) we obtain the familiar Flory-Huggins chemical potential[1]

$$\beta\Delta\mu_1 = \ln \phi_1 + (1 - 1/r)\phi_2 + \chi\phi_2^2 \tag{27}$$

For the polymer chemical potential, eq 22 reduces to a Flory-Huggins potential plus an elastic term $\ln z_{\mathrm{el}}$. However, it can be easily shown that $\alpha^2 = 1$ by eq 18b in this approximation. Thus, $\ln z_{\mathrm{el}} = 0$ and eq 22 also reduces exactly to a FH-type potential.

Notice that our approximation of Ω is tantamount to assuming that mers and solvent are uniformly distributed throughout the solution; i.e., all cells contain exactly λ chains (delta function distribution). Of course, these are the very conditions under which we expect Flory-Huggins chemical potentials to be accurate.

In general, the chemical potentials never reduce exactly to those of the FH type. A better approximation to the chemical potentials can be obtained by carrying the Ω approximation to an additional term to include fluctuations in the number of chains/cell.

D. Osmotic Pressure and Virial Coefficients. The osmotic pressure π of the solution is related to $\Delta\mu_1$ by

$$\beta\pi\sigma^3 = -\beta\Delta\mu_1 = \left(\frac{\phi_2}{r}\right)\frac{\ln \Omega}{\lambda} \tag{28a}$$

Alternatively, eq 28a can be rewritten as

$$\frac{\pi V}{NkT} = \frac{\ln \Omega}{\lambda} \tag{28b}$$

where V is the volume of the system ($V = N_{\mathrm{T}}\sigma^3$; cf. eq A11).

From eq A18 we have

$$\beta\pi\sigma^3 = \frac{\phi_2}{r}[1 + c_2\lambda + c_3\lambda^2 + ...] \tag{29}$$

For a lattice model the virial expansion is of the form

$$\beta\pi\sigma^3 = \frac{\phi_2}{r} + A_2\phi_2^2 + A_3\phi_2^3 + ... \tag{30}$$

where A_2 is a dimensionless second virial coefficient, A_3 is a dimensionless third virial coefficient, etc. Equation 29 can be converted to an expansion in powers of ϕ_2 by expanding λ and the c_n; comparing eq 29 with (30), we find

$$A_2 = c_2(0)/r\phi_\alpha(0) \tag{31}$$

$$A_3 \simeq c_3(0)/r\phi_\alpha^2(0) \tag{32}$$

where it is understood that

$$\phi_\alpha(0) \equiv \lim_{\phi_2\to 0}\phi_\alpha \tag{33}$$

$$c_n(0) \equiv \lim_{\phi_2\to 0} c_n \tag{34}$$

The expression for the third virial coefficient A_3 is very crude because we have ignored contributions to A_3 from the expansion of c_2 and ϕ_α.

From eq A17 we have

$$c_2(0) = \tfrac{1}{2} - e^{-\beta[\Delta A_2(0) - 2\Delta A_1(0)]} \tag{35}$$

and from eq 9

$$\Delta A_2(0) - 2\Delta A_1(0) = r[(1 - \Theta/T)\phi_\alpha(0) + \phi_\alpha^2(0) + ...] \tag{36}$$

where the substitution

$$\Theta/T \equiv 2\chi \tag{37}$$

has been made. Equation 36 represents the free energy change associated with placing two isolated chains into the same cell.

In a good solvent ($\chi \to 0$) we know that $\phi_\alpha(0) \sim r^{-4/5}$ and thus $c_2(0) \to {}^1/_2$. Thus from eq 31, the second virial coefficient is

$$A_2 = [2r\phi_\alpha(0)]^{-1} \sim r^{-1/5} \qquad \text{(good solvent)} \tag{38}$$

The above prediction for the molecular weight dependence of A_2 is not new; it can be arrived at by a very simple and intuitive argument which treats the chains as hard spheres.[3] Also an ample body of experimental evidence supports this result.[18-26]

In a poor solvent near the Θ temperature, $\phi_\alpha(0) \sim r^{-1/2}$. Therefore, from eq 31, we reach the important conclusion that both $c_2(0)$ and $A_2 \rightarrow 0$ at T_0, where

$$(\Theta/T_0 - 1) \sim r^{-1/2} \tag{39}$$

and

$$\lim_{r\rightarrow\infty} T_0 = \Theta \tag{40}$$

This prediction has also been reported before.[27] The physical basis for this result is that ternary interactions become important near the Θ temperature; the $r\phi_\alpha{}^2$ term in eq 36 is the mean-field estimate of the number of ternary mer–mer interactions. This term approaches a constant value as $T \rightarrow \Theta$ and $r \rightarrow \infty$.

At temperatures just above T_0, where $\phi_\alpha(0) \sim r^{-1/2}$, eq 31 yields

$$A_2 \sim r^{-1/2} \qquad \text{(poor solvent)} \tag{41}$$

E. Chain Dimensions in the Dilute Range. Equation 18b can be used to determine chain dimensions in the dilute range ($\lambda < 1$). Combining eq 18b and 8, we obtain

$$\ln \Omega - \beta\phi_\alpha\left\langle \frac{\partial \ln \Delta A_n}{\partial \phi_\alpha} \right\rangle + \lambda(\alpha^2 - 1) = 0 \tag{18c}$$

From eq 9, we have

$$-\beta\phi_\alpha\left\langle \frac{\partial \ln \Delta A_n}{\partial \phi_\alpha} \right\rangle = \frac{r}{\phi_\alpha}\langle \ln (1 - n\phi_\alpha) + (1 - 1/r)(n\phi_\alpha) + \chi(n\phi_\alpha)^2\rangle \tag{42a}$$

Expanding the logarithmic term and then averaging, we obtain

$$-\beta\phi_\alpha\left\langle \frac{\partial \ln \Delta A_n}{\partial \phi_\alpha} \right\rangle = -\left[\lambda + \frac{r\phi_\alpha}{2}(1 - \Theta/T)\langle n^2\rangle + ... \right] \tag{42b}$$

From the definition of λ, eq A8, and eq A14 we have

$$\lambda \equiv \langle n\rangle = \sum_{n=1}^{\infty} nb_n z^n \tag{43}$$

and from the definition of $\langle n^2\rangle$ and eq A17 it is easy to show that the variance, $\langle n^2\rangle - \langle n\rangle^2$, is given by

$$\langle n^2\rangle - \lambda^2 = z\frac{\partial\lambda}{\partial z} = b_1 z - 4c_2(b_1 z)^2 + ... \tag{44a}$$

To obtain z as a function of λ we invert eq 43

$$b_1 z = \lambda + 2c_2\lambda^2 + \tfrac{1}{2}(3c_3 - 4c_2{}^2)\lambda^3 + ... \tag{45}$$

Substituting eq 45 into (44a) yields

$$\langle n^2\rangle = \lambda + (1 - 2c_2)\lambda^2 + ... \tag{44b}$$

Substituting eq A18, 42b, and 44b into eq 18c, we obtain

$$\alpha^2 + 1 + c_2\lambda + c_3\lambda^2 + ... = \frac{r\phi_\alpha}{2}(1 - \Theta/T)\,[1 + (1 - 2c_2)\lambda + ...] \tag{18d}$$

As $\lambda \rightarrow 0$ (infinite-dilution limit), $\alpha \rightarrow \alpha_0$; using eq 2 for ϕ_α, we obtain the well-known Flory excluded-volume equation[15]

$$\alpha_0{}^5 - \alpha_0{}^3 \sim r^{1/2}(1 - \Theta/T) \tag{46}$$

In a good solvent ($T/\Theta \gg 1$) and for large r, we know that $c_2(0) = {}^1/_2$. Using this result in eq 18d and then taking the concentration derivative of α^2, we obtain

$$-D_0 \equiv -\left.\frac{\mathrm{d}\alpha^2}{\mathrm{d}\phi_2}\right|_{\phi_2=0} \sim \frac{r^{1/2}\alpha_0{}^5}{5\alpha_0{}^2 - 3} \sim r^{1/2}\alpha_0{}^3 \sim 1/\phi_\alpha(0) \tag{47}$$

In scaling theories,[7-10] the overlap concentration $\phi_2{}^*$ is defined as that concentration where polymer chains must begin to overlap; in the present notation it is given by

$$\phi_2{}^* \equiv \phi_\alpha(0) \sim r^{-4/5} \qquad \text{(good solvent)} \tag{48}$$

Thus

$$-D_0\phi_2{}^* = \text{positive constant} \qquad \text{(good solvent)} \tag{49a}$$

or equivalently, by using the relationship between A_2 and $\phi_2{}^*$, eq 38, we have

$$-\left.\frac{\mathrm{d}\langle S^2\rangle}{\mathrm{d}\phi_2}\right|_{\phi_2=0} \sim M^2 A_2 \tag{49b}$$

In a poor solvent near the Θ temperature $c_2 \rightarrow 0$; to a first approximation eq 18d yields

$$D_0(T = \Theta) = 0 \tag{50}$$

III. Summary and Discussion

A new theory of polymer solutions has been formulated that is a generalization of the classical theory, i.e., Flory–Huggins theory.[1,2] The generalization is in the direction of accounting for the nonuniform distribution of monomers present in a polymer solution. With a polymer chain treated as a spherical cloud of monomers, the problem of properly accounting for concentration nonuniformities is equivalent to calculating the amount of intermolecular interpenetration (overlap).

To calculate the latter, we use a cell model. The solution volume is divided into cells, each cell just large enough to accommodate a chain with an expansion factor α^2. The cell model can be used to calculate overlap or covolume because we have proved in Appendix B a rather remarkable theorem. It is shown that the process of translating all of the polymer chains to their respective cell centers does not change the mean value of the system's covolume. The translation process creates and destroys covolume, but the effects tend to cancel. Thus, the cell model is a useful artifice for doing the statistical mechanics of interacting polymer chains. However, the model is not exact. The translation or cellularization process conserves the free energy related to intermolecular overlap, but it does not conserve the system's configurational entropy. Limiting molecular centers of mass to cell centers underestimates the volume of configuration space available to the system. The error involved here is similar to that introduced when the lattice gas model is used to represent a hard-sphere fluid.

In general each cell may contain up to m chains, where m is the number of chains that completely fill the cell space. The free energy of a cell containing n chains ($1 \leq n \leq m$) is approximated by a Flory–Huggins free energy. The covolume theorem of Appendix B assumes that the interaction energy or free energy is pairwise additive; i.e., the energy of a cell containing n chains is a quadratic function of n. Using a FH free energy for a cell's free energy is not completely consistent with this pairwise additivity requirement because it contains cubic and higher order terms. However, if the overall polymer volume fraction (ϕ_2) is 0.1 or less, these higher order terms are negligible. For concentrations greater than 0.1 the use of a FH cell free energy is less justifiable but becomes reasonable on other grounds. When it is assumed that every cell has exactly λ chains (delta function distribution), then the solvent and polymer chemical potentials reduce exactly to FH potentials. At concentrations greater than 0.1 the actual distribution is not a delta function but approaches that limit as $\phi_2 \rightarrow 1$. In other words, by using a FH free energy for a cell's free energy, we recover FH chemical potentials at high concentrations. Additionally, in the delta function approximation, it is found that the chains do not swell ($\alpha^2 = 1$). This result is in agreement with the de Gennes argument[3] that concentration uniformity, as assumed in FH theory, implies the absence of chain swelling.

Although cubic and higher order terms are ordinarily negligible for $\phi_2 < 0.1$, the cubic term does become important as $T \rightarrow \Theta$, even in dilute solutions. We feel that retention of at least the cubic term is qualitatively correct near Θ. The presence of this positive term indicates that at $T = \Theta$ the chains are still slightly repulsive; i.e., excluded-volume effects are still present. This situation is analogous to the situation at the Boyle temperature in a real fluid. At the Boyle temperature the second virial coefficient vanishes, but the third virial coefficient does not vanish for either nonpolar or polar fluids.[28] Further, the third virial coefficient is always positive at the Boyle temperature,[28] which indicates that ternary interactions at the Boyle temperature are repulsive. Repulsive ternary monomer interactions near the Θ temperature are responsible for the result that the second virial coefficient (A_2) for a finite molecular weight polymer vanishes slightly below the Θ temperature (see eq 39). Only in the infinite molecular weight limit does A_2 vanish at Θ. This effect should be more pronounced for polymers with bulky side groups or branches. Some experimental evidence in support of this prediction exists.[29]

It was shown that the second virial coefficient A_2 varies with molecular weight as $M^{-1/5}$ in a good solvent ($T \gg \Theta$) and $M^{-1/2}$ in a poor solvent ($T \geq \Theta$). From general considerations $A_2 \sim B/M^2$, where B is the intermolecular excluded volume. If the molecules are highly repulsive, then $B \sim$ molecular volume. For chain molecules, molecular volume $\sim \langle S^2 \rangle^{3/2}$. In a good solvent $\langle S^2 \rangle^{3/2} \sim M^{9/5}$ whereas near the Θ temperature, $\langle S^2 \rangle^{3/2} \sim M^{3/2}$. Therefore, the predicted molecular weight dependence for A_2 is consistent with the notion that the chains tend to strongly repel one another. Near the Θ temperature the repulsion is dominated by ternary monomer interactions. There is an abundant amount of experimental evidence to support the good-solvent prediction,[18-26] but we are unaware of any experimental support for the poor-solvent prediction.

A condition of equilibrium, eq 18, can be used to determine the equilibrium swelling factor α^2 of the chains. In very dilute solutions ($\lambda \rightarrow 0$) this equilibrium condition yields the well-known Flory excluded-volume equation, eq 46. It may surprise some readers that eq 46 emerges from this theory. How were *intra*molecular excluded-volume effects incorporated into the theory? The answer is simple: in very dilute solutions all chains are isolated and the FH free energy of an isolated chain, ΔA_1, includes only intramolecular excluded-volume effects. This has been demonstrated by Sanchez[29] and more recently commented upon by Irvine and Gordon.[5]

Another important prediction of the theory is that even in the dilute regime ($\lambda < 1$) chain dimensions decrease with concentration ($T > \Theta$). Quantitatively, the effect is expressed in eq 47 and 49. Is the effect large? The neutron scattering data of Daoud et al.[8] suggest that it is a sizable effect. In that study the gyration radius of a 1.1×10^5 molecular weight polystyrene in a good solvent decreased from 137 Å at zero concentration to 120 Å at $C = 0.03$ g/cm^3. The latter concentration is well below the estimated overlap concentration of $C^* = 0.075$ g/cm^3. The effect is predicted to be even larger for higher molecular weights.

Difficulties arise in semidilute solutions ($\lambda \gg 1$). The solution free energy begins to exhibit multiple maxima and minima. The minima tend to occur at values of α^2 that make $m = 1/\phi_\alpha$ an integer. This "ripple effect" is an artifact associated with the discrete nature of the cell model. A more serious difficulty, which is the primary shortcoming of the theory, is that calculated concentration fluctuations tend to become very small in the semidilute range. This implies a rapid convergence of the chemical potentials to FH potentials and of α^2 to unity. The reason for this is related to our assumption that "mers" are uniformly distributed within a chain. This assumption is equivalent to ignoring concentration fluctuations on size scales smaller than the average size of the chain. This is clearly an approximation, but it is one that is not easily removed within the context of the cell model.

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Appendix A. General Cell Model

Consider a system of N indistinguishable particles contained in a volume V. We divide the system into ω cells each of volume v_c ($\omega = V/v_c$). The canonical partition function for this system can be expressed as

$$Z = \sum_{\{\omega_n\}} \frac{\omega!}{\prod_{n=0}^{m} \omega_n!} e^{-\beta E\{\omega_n\}} \tag{A1}$$

$$E\{\omega_n\} \equiv \sum_{n=0}^{m} \omega_n E_n \tag{A2}$$

where ω_n is the number of cells containing n particles, m is the maximum number of particles that a cell can accommodate, E_n is the potential energy of a cell containing n particles, and $\beta \equiv (kT)^{-1}$ has its usual meaning. The above sum is over all sets $\{\omega_n\}$ subject to the constraints

$$\sum_{n=0}^{m} \omega_n = \omega \tag{A3}$$

$$\sum_{n=0}^{m} n\omega_n = N \tag{A4}$$

Our assumption that the total potential energy E of the system can be expressed as a sum of cell energies, eq A2, is, in general, invalid for interacting particles. However, in Appendix B we define a class of intermolecular potentials for which this assumption is valid.

In the thermodynamic limit (N, $V \rightarrow \infty$; N/V = constant) we can obtain an excellent approximation to the partition function by determining the most probable values of the cell occupation numbers ω_n; i.e.

$$Z = \frac{\omega!}{\prod_{n=0}^{m} \bar{\omega}_n} \exp[-\beta \sum_{n=0}^{m} \bar{\omega}_n E_n] \tag{A5}$$

where $\bar{\omega}_n$ is the most probable value of ω_n

$$\bar{\omega}_n/\omega \equiv P_n = z^n e^{-\beta E_n}/\Omega \tag{A6}$$

$$\Omega \equiv \sum_{n=0}^{m} z^n e^{-\beta E_n} \tag{A7}$$

The parameter ln z is a Lagrange multiplier used to eliminate the equation of constraint (A4). It is defined by combining eq A4 with eq A6 and A7

$$\lambda \equiv N/\omega = \frac{\partial \ln \Omega}{\partial \ln z} = \sum_{n=0}^{m} nP_n = \langle n \rangle \tag{A8}$$

That is, z is chosen so that the average number of particles/cell equals λ.

The above problem is analogous to the BET adsorption problem.[30] Omitting further details, we now state some useful properties for this model.

Helmholtz Free Energy

$$\beta A = N \ln z - \ln \Omega^{\omega} \tag{A9}$$

Chemical Potential

$$\beta\mu = \ln z \tag{A10}$$

Equation of State

$$\frac{PV}{NkT} = \frac{\ln \Omega}{\lambda} \tag{A11}$$

Cumulant Expansion

$$\Omega = \sum_{n=0}^{m} \frac{a_n}{n!} z^n \tag{A12}$$

where

$$a_n \equiv n! e^{-\beta E_n} \qquad a_0 \equiv 1 \tag{A13}$$

$$\ln \Omega = \sum_{n=1}^{\infty} b_n z^n \tag{A14}$$

where

$$\begin{aligned} b_1 &= a_1 \\ b_2 &= \frac{1}{2!}(a_2 - a_1^2) \\ b_3 &= \frac{1}{3!}(a_3 - 3a_1a_2 + 2a_1^3) \\ b_4 &= \frac{1}{4!}(a_4 - 3a_2^2 - 4a_1a^3 + 12a_1^2a_2 - 6a_1^4) \\ &\dots \end{aligned} \tag{A15}$$

In statistics, $n!b_n$ are known as semiinvariants or cumulants.[31]

Virial Expansion

$$\frac{PV}{NkT} = \sum_{n=1}^{\infty} c_n \lambda^{n-1} \tag{A16}$$

where c_n is the nth virial coefficient defined by

$$\begin{aligned} c_1 &= 1 \\ c_2 &= -b_2/b_1^2 = \tfrac{1}{2}(1 - a_2/a_1^2) \\ c_3 &= -2b_3/b_1^3 + 4b_2^2/b_1^4 \\ c_4 &= -3b_4/b_1^4 + 18b_2b_3/b_1^5 - 20b_2^3/b_1^6 \\ &\dots \end{aligned} \tag{A17}$$

These virial coefficients are formally identical with those for an imperfect gas.[32]

Notice that when eq A11 and A16 are combined, we obtain ln Ω as a power series in λ

$$\ln \Omega = \sum_{n=1}^{\infty} c_n \lambda^n \tag{A18}$$

Appendix B. Covolume Theorem

Theorem. Consider a system of N spherical particles of diameter d whose potential energy is pairwise additive. The system is divided into ω cells each of volume $(\pi/6)d^3$. A system configuration in which all N sphere centers are at cell centers is defined as a cellular configuration. Any system configuration can be converted to a cellular configuration by translating all spheres which are located at off-center positions to the centers of their respective cells. If the pair potential $u(s)$ between spheres separated by a distance s is proportional to the covolume, i.e., if

$$\begin{aligned} u(s) &= u_0(1 - s/d)^2(1 + s/2d) \qquad s < d \\ &= 0 \qquad s \geq d \end{aligned}$$

then the mean potential energy of the system, $\langle E \rangle$, is equal to the mean potential energy of the cellular system, $\langle E \rangle_{\text{cell}}$

$$\langle E \rangle = \langle E \rangle_{\text{cell}} = \omega \langle E_k \rangle = \frac{\omega u_0}{2} \langle k(k-1) \rangle$$

where E_k is the energy of a cell containing k spheres with $k(k-1)/2$ pair interactions.

Proof. Assuming pairwise additivity and a spherically symmetric pair potential, the mean potential energy of the system in the thermodynamic limit can be expressed as

$$\langle E \rangle = \frac{N\rho}{2} \int g(s)u(s)\, \mathbf{ds} \tag{B1}$$

where

$$s \equiv |\mathbf{s}| \equiv |\mathbf{R} - \mathbf{R}'| \tag{B2}$$

is the distance between spheres located at $\mathbf{R}$ and $\mathbf{R}'$, $\rho = N/V$ is the mean number density, and $g(s)$ is the dimensionless *pair distribution function* defined in terms of the *molecular pair distribution function* $n(s)$

$$g(s) \equiv n(s)/\rho^2 \tag{B3}$$

$n(\mathbf{R},\mathbf{R}')\, \mathbf{dR}\, \mathbf{dR}'$ is proportional to the probability of finding a sphere center at $\mathbf{R}$ in a volume element $\mathbf{dR}$ and another sphere center at $\mathbf{R}'$ in a volume element $\mathbf{dR}'$ irrespective of the positions of the remaining $N - 2$ spheres. Since $u(s)$ is spherically symmetric, $n(\mathbf{R},\mathbf{R}') \rightarrow n(s)$ in the thermodynamic limit.

The Fourier transform (FT) of $g(s)$ is $\tilde{g}(q)$ and is defined by

$$\tilde{g}(q) \equiv \int e^{i\mathbf{s}\cdot\mathbf{q}} g(s)\, \mathbf{ds} \tag{B4}$$

and its inverse by

$$g(s) \equiv (2\pi)^{-3} \int e^{i\mathbf{s}\cdot\mathbf{q}} \tilde{g}(q)\, \mathbf{dq} \tag{B5}$$

Thus, eq B1 can be rewritten as

$$\langle E \rangle = (2\pi)^{-3} \left(\frac{N\rho}{2} \right) \int \mathbf{dq}\, \tilde{g}(q) \int e^{-i\mathbf{s}\cdot\mathbf{q}} u(s)\, \mathbf{ds}$$

$$\langle E \rangle = (2\pi)^{-3} \left(\frac{N\rho}{2} \right) \int \tilde{g}(q)\tilde{u}(q)\, \mathbf{dq} \tag{B6}$$

where $\tilde{u}(q)$ is the FT of $u(s)$.

For the system partitioned into ω cells, we have

$$\langle E \rangle_{\text{cell}} = \omega \sum_{k=0}^{m} P_k E_k \tag{B7}$$

where P_k is the probability of having k spheres in a cell of volume $(\pi/6)d^3$ and E_k is the potential energy of a cell containing k spheres. Since there are $^1/_2k(k-1)$ pair interactions/cell and all spheres have been translated to their respective cell centers, we have

$$E_k = \tfrac{1}{2}k(k-1)u_0 \tag{B8}$$

where u_0 is the value of the pair potential when $s = 0$. Thus, eq B7 becomes

$$\langle E\rangle_{\text{cell}} = \frac{\omega u_0}{2}[\langle k^2\rangle - \langle k\rangle] \tag{B9}$$

Now

$$k = \sum_{i=1}^{N} \int_{v_c} \delta(\mathbf{R} - \mathbf{R}_i)\, \mathrm{d}\mathbf{R} \tag{B10}$$

where the above integration is over the volume of a cell, $v_c = (\pi/6)d^3$, and $\delta(\mathbf{x})$ is a three-dimensional delta function. We also have

$$k^2 = \sum_{i=1}^{N}\sum_{j=1}^{N} \int_{v_c}\int_{v_c} \delta(\mathbf{R} - \mathbf{R}_i)\delta(\mathbf{R}' - \mathbf{R}_j)\, \mathrm{d}\mathbf{R}\, \mathrm{d}\mathbf{R}' \tag{B11}$$

and therefore

$$\langle k^2\rangle - \langle k\rangle = \Big[\sum_{i\neq j}\sum_{i\neq j}\int_{v_c}\int_{v_c} \mathrm{d}\mathbf{R}\, \mathrm{d}\mathbf{R}' \int\int n(\mathbf{R}_i,\mathbf{R}_j)\delta(\mathbf{R} - \mathbf{R}_i)\delta(\mathbf{R}' - \mathbf{R}_j)\, \mathrm{d}\mathbf{R}_i\, \mathrm{d}\mathbf{R}_j\Big] \Big/ \Big[\sum_{i\neq j}\sum_{i\neq j}\int\int n(\mathbf{R}_i,\mathbf{R}_j)\, \mathrm{d}\mathbf{R}_i\, \mathrm{d}\mathbf{R}_j\Big]$$

or

$$\langle k^2\rangle - \langle k\rangle = \int_{v_c}\int_{v_c} n(\mathbf{R},\mathbf{R}')\, \mathrm{d}\mathbf{R}\, \mathrm{d}\mathbf{R}' \tag{B12}$$

Using eq A3 and introducing the FT of $g(s)$, we obtain

$$\langle k^2\rangle - \langle k\rangle = (2\pi)^{-3}\rho^2 \int \mathrm{d}\mathbf{q}\, \tilde{g}(q) \int_{v_c}\int_{v_c} e^{-i\mathbf{q}\cdot\mathbf{s}}\, \mathrm{d}\mathbf{R}\, \mathrm{d}\mathbf{R}'$$

Assuming that v_c has an inversion center ($\mathbf{R} \leftrightarrow -\mathbf{R}$), we have

$$\langle k^2\rangle - \langle k\rangle = (2\pi)^{-3}\rho^2 \int \mathrm{d}\mathbf{q}\, \tilde{g}(q)\Big[\int_{v_c} e^{i\mathbf{q}\cdot\mathbf{R}}\, \mathrm{d}\mathbf{R}\Big]^2 \tag{B13}$$

Since the pair potential is spherically symmetric, the shape of the volume v_c (cube, sphere, etc.) over which the above integration is performed is unimportant; its specific location in V is also unimportant in the thermodynamic limit. Choosing v_c to be a sphere of diameter d gives the integral over $\mathbf{R}$ in eq B13 equal to the FT of $H(d/2 - |\mathbf{R}|)$, where $H(x)$ is a unit step function

$$\begin{aligned} H(x) &= 1,\ x > 0 \\ &= 0,\ x \leq 0 \end{aligned} \tag{B14}$$

Combining eq B9 and B13, we obtain

$$\langle E\rangle_{\text{cell}} = (2\pi)^{-3}\frac{\omega u_0}{2}\rho^2 \int \mathrm{d}\mathbf{q}\, \tilde{g}(q)\{\mathrm{FT}[H(d/2 - |\mathbf{R}|)]\}^2 \tag{B15}$$

Comparing eq B15 and B6, we see that $\langle E\rangle = \langle E\rangle_{\text{cell}}$ if, and only if

$$\tilde{u}(q) = \frac{u_0}{(\pi/6)d^3}\{\mathrm{FT}[H(d/2 - |\mathbf{R}|)]\}^2 \tag{B16}$$

Using the convolution theorem for transforms, we rewrite eq B16 as

$$\tilde{u}(q) = \frac{u_0}{(\pi/6)d^3}\mathrm{FT}\Big[\int H(d/2 - |\mathbf{R}'|)H(d/2 - |\mathbf{R}' - \mathbf{R}|)\, \mathrm{d}\mathbf{R}'\Big] \tag{B17}$$

The simple geometric interpretation of the integral on the right-hand side of eq B17 is that it equals the covolume between two spheres, both of diameter d, located at $\mathbf{R}$ and $\mathbf{R}'$. Therefore, inverting B17 yields

$$u(s) = u_0 \text{ covolume/volume}$$

$$u(s) = u_0(1 - s/d)^2(1 + s/2d) \tag{B18}$$

Q.E.D.

The above potential is a soft potential if u_0 is of the order of kT or less; i.e., configurations involving complete overlap ($s = 0$) will be relatively probable even for $\lambda < 1$. If $u_0 \gg kT$, then the potential effectively behaves as a hard-core potential. Other statistical mechanical models that employ similar "soft potentials" include the Gaussian core model of Stillinger[33,34] and the penetrable-sphere model of Widom and Rowlinson.[35] The latter model superficially resembles the present model, but it is unique in that the system potential is not pairwise additive. This nonadditivity property has the effect of producing an effective hard core to an otherwise attractive potential. In the Gaussian core model, the pair potential is of the form

$$u_0 e^{-(s/d)^2}$$

At small values of s/d our potential, eq B18, is by comparison a simple exponential

$$u_0 e^{-3/2(s/d)}$$

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