AVERAGE CONFIGURATION OF FINITE POLYMER WITH EXCLUDED VOLUME INTERACTION

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A quasi-thermodynamic model for expansion of polymer configuration in solution is investigated. The model is based on Gaussian distribution of segments and mean field theory of polymer solution. An in-homogeneous contribution to the free energy of solution is proposed. It arises from the nonhomogeneous distribution of polymer segements. This effects makes the expansion factor α to be larger than those without the effect considered. Some numerical consequence for the case Polydimethylsiloxane+cyclohexane solution is calculated. Our theory predicts a larger value a than the case without inhomogeneous effect being considered. The difference becomes less significant at higher molecular weight.

Theoretical description of dilute polymer solution requires a knowledge of the average configuration of the polymer. Usually, the average configuration is characterized by the mean square radius of gyration

$$\langle S^2\rangle=\frac{1}{n}\sum_i\langle s_i^2\rangle$$

where s_i is the distance of the i'th segment to the center of mass of the polymer. More complete information involves the distribution $P(S)$ for S.

There are two factors in the determination of average configuration of polymer, (a) free energy of mixing of polymer segments in solvent, it depends on the "goodness" of the solvent (b) elastic free energy of the polymer configuration distribution. These two opposite factors balance each other to determine the average configuration of the polymer. In (a) and (b), one of the important effect is the so-called excluded volume problem. It arises from long range interaction between far-apart segments of the polymer. Flory[1~2] treated this problem first, he used a quasi-thermodynamic approach that considers the two opposite effects mentioned above. Later, there are many workers investigate this problem via more sophisticated statistical mechanics[3~4]. Basically most of the previous works deal with the expansion of random coil in the infinite mass limit and a relation as in Eq (1) is sought

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

with $\langle S^2\rangle_0$=average extension of Gaussian coil at θ-state which is assumed to have no net excluded volume interactions. Excluded volume makes α depends on molecular weight and polymer-solvent interaction. In previous approaches[1], the polymer is taken as an infinitely long chain that polymer extension can be treated uniformly. In the free energy expression, such effect depends only on local segment density. In real polymer of finite length, the excluded volume effect must lead to the most pronounced changes in the central region of the coil, where segment density is highest. In the fringe region, where polymer-solvent interface effect would make the excluded volume contribution to be different.

Schematically, the fringe segments of the polymer has different environment from the center segments. We shall take this into consideration by adding a density gradient term

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in free energy expression, this is shown to be consistent with modern theory of inhomogeneous system[5], in particular, the theory of polymer interface[6~7]. The effect is to have less density gradient and as a result, the distribution function of radius of gyration tends to become sharper than in the unperturbed random flight chain. Also the expansion factor α becomes larger than Flory's theory, at lower molecular weight. However, such effect is usually negligible for high molecular weight polymer far from θ-state due to the small surface-to-volume ratio. It will become significant when polymer molecular weight is low and near θ-state.

Vrij[8] had considered such an inhomogeneous contribution to the expansion factor α. An important result of the contribution is that at θ-temperature, α is not equal to unity as before, but somewhat larger. Later Casassa[9] considered its effect on branched polymer chains in solution; he concluded that the effect is not important. Candau[10] and coworkers put Vrij's theory to experimental test and indicated the shortfalls of Vrij-Casassa theory. The comparisons with experiments were mainly with variation on temperatures.

It is the purpose of this paper to reexamine the effect based on a different derivation and considered the inhomegeneous effect for very short polymer chains (molecular weight down to 10^4). We will examine the effect for the case polydimethylsiloxane+cyclohexane. We show that for very low molecular weight the inhomogeneous contribution to free energy is not neglegible.

THEORY

In the ideal state where excluded volume interactions can be neglected and chain is infinitely long, we consider the Gaussian distribution of random coil,

$$P_0(S)=4\pi S^2\left(\frac{3}{2\pi\langle S^2\rangle_0}\right)^{3/2}\cdot\exp\left(-\frac{3S^2}{2\langle S^2\rangle_0}\right) \qquad (2)$$

as an reference state. It will serve as a point of departure for the present treatment as in Flory's theory. If we consider a chain of n elements, then only a fraction $f(S)$ of the random flight configurations which corresponds to a fixed S will be allowed when the excluded volume is other than zero. The distribution for the real chain will be

$$P(s)=\frac{f(s)\ P_0(s)}{\int_0^\infty f(s)\ P_0(s)\ ds} \qquad (3)$$

Then we wish to calculate the function $f(s)$. We will take the mean field approach as Flory, let us assume $V(s)$ to be the intramolecular potential of mean force with S fixed. Then,

$$f(s)=\exp(-V(s)/K_BT) \qquad (4)$$

$V(s)$ will be the free energy of the polymer coil interacting with solvent, with the polymer center of mass fixed in space.

Let $\rho(s|S)d^3s$ to be the probability of finding any one of the n segments in the volume element d^3s at the distance s from the center of mass with S fixed, we have

$$\int\rho(s|S)d^3s=n \qquad (5)$$

Let V_s to be the volume of the polymer segment, volume density of polymer segment $\phi(s/S)$ will be

$$\phi(s/S)=V_s\,\rho(s/S) \qquad (6)$$

In the mean field approach, $V(s)$ will be a functional of volume density $\phi(s/S)$, it can be expressed as

$$V(s)=\int g[\phi(s/S)]\ d^3s \qquad (7)$$

where $g[\phi]$ is the local free energy of the polymer segments. We will assume that local density and its gradient are small so that free energy density can be expanded as a Taylor series

$$\begin{aligned} g(\rho, \nabla\rho, \nabla^2\rho, \cdots) \\ = g_0(0) + g^{(1)}(0)\rho + 1/2g^{(2)}(0)\rho 2 \\ + \ell\nabla\rho + k_1(\nabla\rho)^2 + k_2\nabla^2\rho + \cdots \end{aligned} \tag{8}$$

with

$$g^{(1)}(0) = \frac{\partial g}{\partial\rho}\bigg|_{\rho=0} \qquad g^{(2)}(0) = \frac{\partial^2 g}{\partial\rho^2}\bigg|_{\rho\sim 0}$$

$$k^1 = \frac{1}{2}\,\frac{\partial^2 g}{\partial(\nabla\rho)^2} \qquad k^2 = \frac{\partial g}{\partial\nabla^2\rho}$$

Such kind of density expansion is well-known in the theory of fluid interface(5,11). Of the coefficients, ℓ must be zero because the polymer is spherically symmetric, the free energy must be invariant to the symmetry operation of $X_i \to -X_i$. The first and second terms in Eq (8) will give constant contributions (independent of S), upon integration, to $V(s)$; so they can be taken as zero. Thus we have

$$V(S) = \frac{1}{2} g^{(2)}(0) \int [\rho(s|S)]^2 d^3s + \int k_1(\nabla\rho)^2\, d^3s + \int k_2\, \nabla^2\rho\, d^3s$$

By applying the divergence theorem to the last term and the surface term is zero in the integration by parts.
We can write

$$V(S) = \frac{1}{2} g^{(2)}(0) \int [\rho(\,|S)]^2\, d^3s + \int k(\nabla\rho)^2\, d^3s \tag{9}$$

with

$$k = k_1 - \frac{\partial k_2}{\partial\rho}$$

with the truncation of higher order terms. It will be shown later that k is density independent to first approximation. We should note here that the density gradient term in Equation (9) is absent in previous theories. The evaluations of the coefficients $g^{(2)}(0)$ and k require statistical thermodynamic models, we shall delay this until next section

The complete form of $\rho(s|S)$ is still poorly known at present12~13, and we shall approximate it by a Gaussian function. Since by definition

$$S^2 = n^{-1} \int s^2 \rho(s|S) d^3s \tag{10}$$

The Gaussian function satisfying this condition is

$$\rho(s|S) = n\left(\frac{3}{2\pi S^2}\right)^{3/2} \cdot \exp\left(-\frac{3s^2}{2S^2}\right) \tag{11}$$

With Equation (11), one can evaluate $V(s)$. The result is

$$V(S) = \frac{3^{3/2}}{16\pi^{3/2}}\, n^2 g^{(2)}(0) S^{-3} + \frac{3^{7/2}}{16\pi^{3/2}}\, n^2\, k\, S^{-5} \tag{12}$$

and the distribution function is

$$P(S) = \frac{P_0(S) \exp\left(-V(S)/K_BT\right)}{\int_0^\infty P_0(S) \exp\left(-V(S)/K_BT\right) dS} \tag{13}$$

Defining

$$x = S/\langle S^2\rangle_0^{1/2} \tag{14}$$

$$V(x) = Ax^{-3} + Bx^{-5} \tag{15}$$

$$A = \frac{3^{3/2}}{16\pi^{3/2}}\ \frac{n^2 g^{(2)}(0)}{\langle S^2\rangle_0^{3/2}} \tag{16}$$

$$B = \frac{3^{7/2}\, n^2\, k}{16\pi^{3/2} \langle S^2\rangle_0^{5/2}} \tag{17}$$

The squared expansion factor α^2 may be calculated from

$$\alpha^2 = \frac{\langle S^2\rangle}{\langle S^2\rangle_0} = \frac{\int_0^\infty x^4 \exp\left(-\frac{3x^2}{2} - \frac{V(x)}{K_BT}\right) dx}{\int_0^\infty x^2 \exp\left(-\frac{3x^2}{2} - \frac{V(x)}{K_BT}\right) dx} \tag{18}$$

The ratio of the two integrals in Eq (18) may be evaluated approximately following the procedure of Herman and Overbeek[14], the approximate value of α is equal to the value x at which $x^3 \exp\left[-\frac{3x^2}{2}-V(x)/K_BT\right]$ is a maximum. That is,

$$\frac{\partial}{\partial\alpha}\left[\ln\alpha^3-\frac{3}{2}-\frac{V(\alpha)}{K_BT}\right]=0 \qquad (19)$$

or

$$\alpha^5-\alpha^3=\frac{A}{K_BT}+\frac{5B}{3K_BT}\alpha^{-2} \qquad (20)$$

Both A and B are molecular weight dependent. It will be shown in the next section that $A \infty M^{1/2}$ and $B \infty M^{-1/2}$. When M approaches infinite, Eq (20) reduces to the result of Flory

$$\alpha^5-\alpha^3=\frac{A}{K_BT} \qquad (21)$$

FREE ENERGY OF POLYMER COIL

In this section, we will present a model calculation of $V(S)$. The purpose is for a qualitative understanding of the relative contribution of both terms, rather than quantitative precision. As indicated before, the value of $g^{(2)}(0)$ and k require free energy model for the polymer-solvent mixture. Here we will adopt the Flory-Huggins model[15~16].

For a uniform distribution of polymer system, the free energy density is expressed in terms of volume fraction ϕ. According to Flory-Huggins Theory, for a polymer of n segments with solvent molecular volume V_0, the free energy per unit volume is

$$g=\frac{K_BT}{V_0}\left[(1-\phi)\ln(1-\phi)+\frac{\phi}{n}\ln\phi+\chi\phi(1-\phi)\right] \qquad (22)$$

Where χ is the interaction-parameter representing enthalpy change of mixing. For long polymer $n \gg 1$, usually the second term in the bracket can be neglected. Eq (22) becomes

$$g=\frac{K_BT}{V_0}[(1-\phi)\ln(1-\phi)+\chi\phi(1-\phi)] \qquad (23)$$

Thus

$$\begin{aligned} g^{(2)}(0)&=V_s^2\frac{\partial^2 g}{\partial\phi^2}\\ &=\frac{2V_s^2K_BT}{V_0}\left(\frac{1}{2}-\chi\right)\\ &=\frac{2V_s^2K_BT}{V_0}\Psi(1-\Theta/T) \qquad (24)\end{aligned}$$

Where Ψ is the entropy parameter, Θ is the theta temperature.

For the coefficient, k, we need a theory of inhomogeneous system applied to polymer distribution. It comes from nonlocal contribution to the free energy of inhomogenous fluid system as stressed by Cahn and Hilliard[5], Landau and Lifshitz[17], Debye[18] and recently by Helfand[6~7]. In the following, we follow Helfand's approach.

Within Flory's quasi-lattice model of polymer-solvent system, we shall determine the enthalpy of non-uniform system. Let $C(R)$ and $C(S)$ be the probabilities of finding a B molecule solvent at site R and A-segment at site S. The probability P_{AB} of finding such A, B pair is

$$P_{AB}=C(R)[1-C(S)]\,g_{AB} \qquad (25)$$

Where g_{AB} is the pair correlation. Assuming that g_{AB} is independent of density, we than expand $C(S)$ around R as

$$\begin{aligned} C(S)&=C(R)+(\mathbf{r}\cdot\nabla)C(R)\\ &\quad+\frac{1}{2}(\mathbf{r}\cdot\nabla)^2C(R) \qquad (26)\end{aligned}$$

$\mathbf{r}$, being the distance between R and S.

Let $\nu(r)=E_{AB}-1/2(E_{AA}+E_{BB})$, where E's are the intermolecular potential for polymers, polymer-solvent, solvent-solvent interactions. We find that the total energy per molecule at R, $U(R)$, relative to the pure component is:

$$U(R)=C(R)[1-C(R)]\int g_{AB}(r)\,\nu(r)\,d^3r$$
$$-\left[\frac{1}{6}\int g_{AB}(r)\,\nu(r)\,r^2\,d^3r\right]C(R)\,\nabla^2 C(R) \tag{27}$$

Where the ∇c term vanishes due to spheral symmetry. The coefficient of the $\nabla^2 c$ term can be further written as

$$U(R)=\omega\,C(R)[1-C(R)]$$
$$-\frac{\omega\lambda^2}{2}C\,\nabla^2 c(R) \tag{28}$$

with

$$\omega=\int g_{AB}(r)\,\nu(r)\,d^3r \tag{29}$$

$$\lambda^2=\frac{\int g_{AB}(r)\,\nu(r)r^2\,d^3r}{3\int g_{AB}(r)\,\nu(r)\,d^3r} \tag{30}$$

Hence ω will be related to the well-known χ parameter of Flory as

$$\omega=K_BT\,\chi \tag{31}$$

λ has the dimension of length and represents a root-meansquare interaction distance. For Flory's model, one can simply write the free energy density as

$$g=g_0-\frac{\omega\lambda^2}{2V_0}\phi\,(\nabla^2\phi) \tag{32}$$

with the replacement of c by local volume fraction ϕ. Identifying,

$$k_1=0, \qquad k_2=-\frac{\omega\lambda^2\,V_s^2\,\rho}{2V_0},$$

We now have from Eq (9)

$$k=\frac{\omega\lambda^2\,V_s^2}{2V_0} \tag{33}$$

Finally, with Eq (16), (17), we have

$$A=\frac{3^{3/2}\bullet 2n^2\,V_s^2\,K_BT(\frac{1}{2}-\chi)}{16\pi^{3/2}\,\langle S^2\rangle_0^{3/2}\,V_0} \tag{34a}$$

$$B=\frac{3^{7/2}\bullet(n^2\,V_s^2\,K_BT\,\lambda^2\,\chi)}{32\pi^{3/2}\,\langle S^2\rangle_0^{5/2}\,V_0}$$

Recalling that $n\,V_s=M\,\overline{V}/N_A$, with N_A the Avagadro number, M the polymer molecular weight, and $\overline{V}$ the polymer partial specific volume, we may also write

$$A=\frac{3^{3/2}}{8\pi^{3/2}}\left(\frac{M}{\langle S^2\rangle_0}\right)^{3/2}\frac{\overline{V}^2\,K_BT(\frac{1}{2}-X)}{N_A^2\,V_0}M^{1/2} \tag{35a}$$

$$B=\frac{3^{7/2}}{32\pi^{3/2}}\left(\frac{M}{\langle S^2\rangle_0}\right)^{5/2}\frac{\overline{V}\,K_BT\,\chi\,\lambda^2}{N_A^2\,V_0}M^{-1/2} \tag{35b}$$

It is interesting to note the ratio A/B,

$$\frac{A}{B}=\left(\frac{4}{9}\right)\frac{\langle S^2\rangle_0(\frac{1}{2}-\chi)}{\lambda^2\,\chi} \tag{36}$$

One can see that from Eq (35), as the molecular weight of polymer increases the contribution of inhomogeneous term becomes less important. This is due to the rapid decrease of "surface area" of polymer coil. In general, λ is expected to be of the magnetude of segment length and $\langle S^2\rangle_0/\lambda^2$ is expected to be much less than one. Only in the case χ is close to 1/2 would B-term in $V(S)$ be significant compared to A-term. That is, close to θ point, the deviation from random coil behavior could be attributed to the inhomogeneous effect.

RESULTS AND DISCUSSIONS

In section (III) and (IV), we have developed a quasithermodynamic theory of polymer configuration expansion under excluded volume interaction. The result depends on many thermodynamic parameters. We want in this section to examine some numerical consequences for some typical polymer solutions in order to compare the relative importance of individual terms. We want to see, specifically, how the distribution function $P(S)$ and expansion factor α are altered upon consideration of the surface excluded volume effect for a finite polymer.

In Table 1, we list the relevant structural

Table 1. Resume of Thermodynamic parameters for represntative polymer solutions[c]

Polymer+solvent[a]	$[\langle S^2\rangle_0/M]\times10^{18}$ (cm^2/g)	$\overline{V}$ (cm^3/g)	N_AV_0 ($cm^3/mole$)	$\chi(25°C)$[d]	$10^8\times\lambda$ (cm)
PS+C-C_6H_{12}	8.0	0.9293	108	0.505	6.6
PDMS+C-C_6H_{12}	6.2	1.05	108	0.42	5.8
NR+C_6H_6	11.5[b]	1.10[b]	89	0.42	8.0

a. PS=Polystyrene, PDMS=Polydimethylsiloxane, NR=Natural Rubber.
b. Estimated from other temperature.
c. All data than χ obtained from "Polymer Handbook" edited by J. Brandrup and E. H. Immergut (Interscience, New York, 1966).
d. χ from reference (19).

Table 2. $V(x)$ parameters for PDMS+cyclohexane at several molecular weight (25°C)

$M=10^4$	5×10^4	10^5	2×10^5	5×10^5	10^6
$A/K_BT=1.02$	2.29	3.24	4.58	7.25	10.2
$B/K_BT=0.657$	0.294	0.208	0.147	0.093	0.066

and thermodynamic parameters for the polymer solution system: Polystyrene+ cyclohexane, polydimethylsiloxane +cyclohexane and natural rubber+benzene. All the data are obtained from "Polymer Handbook" edited by Brandrup and Immergut. Of these parameters, the segment interaction distance λ is least known. However, as one expects, λ represents the range of interaction; so here we simply take λ to be the segment length. This should be a reasonable estimate barring exceptional long range force.

From the data in Table 1, one can calculate the A, B parameters in our theory, using Eq (35). We will examine here first the relative importance of A term and B term. We chose the system PDMS+cyclohexane at 25°C, the values of A and B are listed in Table 2. One can see that A is always larger than B; the contribution of inhomogeneous free energy is relatively small at large molecular weight but becoming more significant at smaller molecular weight.

Let us first examine the distribution function $P(S)$, for three cases:

(a) Idea Gaussian chain with no excluded volume

$$P_1(x)=\frac{e^{-3/2(x^2)}\ x^2}{\int_0^\infty e^{-3/2(x^2)}\ x^2\ dx} \tag{37}$$

(b) The original Flory model with excluded volume, eg. $B=0$

$$P_2(x)=\frac{x^2\ e^{-3/2(x^2)-Ax^{-3}}}{\int_0^\infty x^2\ e^{-3/2(x^2)-Ax^{-3}}\ dx} \tag{38}$$

(c) This work, with surface term included

$$P_3(x)=\frac{x^2\ e^{-3/2(x^2)-Ax^{-3}-Bx^{-5}}}{\int_0^\infty x^2\ e^{-3/2(x^2)-Ax^{-3}-Bx^{-5}}\ dx} \tag{39}$$

We calculate these distribution functions for PDMS at 25°C and $M=10^4$ while the effect of B-term is more important. The result is shown in Fig. 1. As expected, the effect of excluded volume is to shift the distribution toward larger extension and narrower. The effect of surface term is to shift $P_3(x)$ even more. B term is not negligible in this case. As the molecular weight increases, surface term becomes less important, for $M=10^6$, $P_2(x)$ and

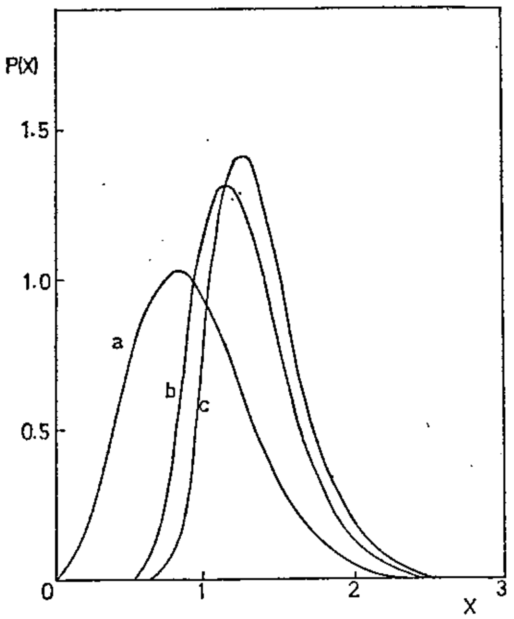

Fig. 1. Distribution function for radius of gyration of polymer. a: without exclude volume interaction $V(x)=0$, b: $A/K_BT=1.02$ $B=0$. c: $A/K_BT=0.657$ (This work).

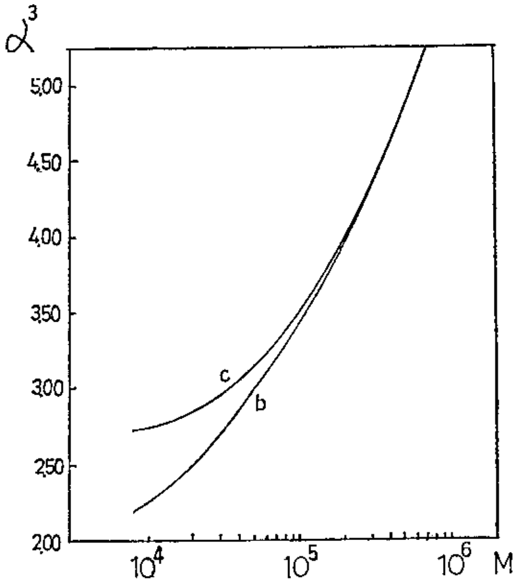

Fig. 2. Volume expansion factor α^3 Vs. M. The case is for PDMS+cyclohexane at 25°C. b: From Flory's theory, c: from this work with $B\neq 0$.

$P_3(x)$ are almost identical.

Next, we calculate the value α using the two distribution functions $P_2(x)$ and $P_3(x)$. Experimentally, one measures α^3 (volume expansion factor). So we plot α^3 versus M in Fig. 2 for PDMS at 25°C. One can see here α^3 increases as M increases. Our theory here predicts a larger α than Flory's theory (curve b), the difference is larger at lower molecular weight, tending toward zero at higher molecular weight.

From the above numerical examples, we conclude that the original Flory's theory of excluded volume effect is probably justified in neglecting the inhomogeneous free energy effect at high molecular weight. However, at lower molecular weight this effect may not be neglected, as seen from this model study. One must be aware that, the Gaussian distribution used in this work is not an accurate representation of the real polymer, especially for $\rho(s/S)$. In more realistic $\rho(s/S)$, one may encounter sharper gradient of density and, in that case, the contribution of inhomogeneous free energy could become more significant. Previously, Fixman[12] did evaluate the function $\rho(s/S)$ for larger S of an ideal chain, he found that there is a very sharp boundary to the molecule in the distribution of segments. In this case, the gradient term in our theory theory should smooth the distribution out.

To summarize, we have constructed a quasithermodynamic model for the excluded volume effect of polymer configuraiton. The model study indicates that the inhomogeneous free energy makes the polymer extend out more in good solvent than Flory's theory, and the effect become less important at higher molecular weight. Although we have derived the theory based on Gaussian distributions and mean field theory, we believe the qualitative conclusion is correct.

In order to examine closer the experimental implications, more work on more realistic model is desirable.

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REFERENCES

(1) P. J. Flory, *J. Chem. Phys.* **17**, 303 (1949).

(2) P. J. Flory and T. G. Fox, *J. Am. Chem. Soc.* **73**, 1904 (1951).

(3) H. Morawetz, "Macromolecules in solution" 2nd ed, A. P. (1974).

(4) H. Yamakawa, "Modern Theory or Polymer Solutions" Haper and Row, (1971).

(5) J. W. Cahn and J. E. Hilliard, *J. Chem. Phys.* **28**, 258 (1958).

(6) E. Helfand and Y. Tagami, *J. Chem. Phys.* **56**, 3592 (1972).

(7) E. Helfand, *Acct. of Chem. Res.* **8**, 295 (1975).

(8) A. Vrij, *J. Polymer Sci.* Part A-2, Vol. 7, 1627 (1969).

(9) E. F. Casassa, *J. Polymer Sci.* Part A-2, Vol. **8**, 1651 (1970).

(10) F. Candau, P. Rempp and H. Benoit, *Macromolecules*, **5**, 627 (1972).

(11) H. L. Frish and J. L. Lebowitz, "the Equilibrium Theory of Classical Fluids" (Benjamin, N. Y) (1964).

(12) M. Fixman, *J. Chem. Phys.* **36**, 3123 (1962).

(13) B. E. Eichinger, *Macromolecule.* **13**, 1 (1980).

(14) J. J. Hermans and J. Th. G. Overbeek, *Rec. Trav. Chim.* **67**, 761 (1948).

(15) P. J. Flory, "Principle of Polymer Chemistry" Cornell University Press, Ithaca, New York, (1953).

(16) M. L. Huggins, *J. Phys. Chem.* **46**, 151 (1942); *Ann. N. N. Acad. Sci.* **41**, 1 (1942).

(17) L. D. Landau and E. M. Lifshitz, "Statistical Physics" Pergamon, London (1958).

(18) P. Debye, in "Non-Crystslline Solide" edited by V. D. Frechette, Wiley, New York, (1960).

(19) P. J. Flory, *Diss. Faraday Soc.* **59**, 7 (1970).

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