An Unsophisticated Calculation of the Excluded Volume Exponent

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The space-filling quality of the elements of a flexible chain polymer molecule induce a singular perturbation in the statistics of the chain configuration. The "self-avoiding walk" or "excluded volume" effect, the name given to this problem, is widely celebrated, and no exact solutions have been offered.[1-9] The problem derives its importance from two sources. First of all, the physical properties of polymers and polymer solutions are intimately connected with chain statistics, and the excluded volume constitutes an ever-present difficulty. Second, the excluded volume problem is a challenge to the mathematician, it contains elements which lie beyond the boundaries of the well known in mathematical probability, and this quality, irrespective of practical consequences, has attracted a number of interested researchers.

We offer here another approximate calculation which arrives at an old result in a new way. The method is simple and direct, the assumptions are clearly stated, and the calculation is internally consistent.

The Excluded Volume Model

A flexible polymer molecule containing N freely rotating monomer units of length b obeys a Gaussian probability law for large N in the absence of excluded volume. In the presence of a volume effect, this probability is modified by short-range repulsion forces between all pairs of monomer units. The probability that the chain ends are separated by R may be written as

$$P(\mathbf{R}) = \Omega(\mathbf{R}) \exp[-H(\mathbf{R})/hT]/Z \tag{1a}$$

$$\Omega(\mathbf{R}) = \exp[-3R^2/2Nb^2] \tag{1b}$$

$$Z = \int \Omega(\mathbf{R}) \exp[-H(\mathbf{R})/hT]\, \mathrm{d}\mathbf{R} \tag{1c}$$

$\Omega(\mathbf{R})$ originates in the polymer statistics in the absence of excluded volume. $H(\mathbf{R})$ is the repulsive energy between all segment pairs and may be written as a double sum

$$H(\mathbf{R}) = \frac{1}{2}\sum_{i,j=1}^{N} h_{ij}(\mathbf{R}) \tag{2}$$

$h_{ij}(\mathbf{R})$ is the repulsive energy between the ith and jth monomer. We omit local interactions of constant bond angle and restricted rotation since they play no role in the problem, and their introduction would only obscure matters of interest.

The repulsive energy between a pair of segments is approximated by a "mean field" argument. $h_{ij}(\mathbf{R})$ is zero unless units i and j occupy a common volume. When they do occupy a common volume, $h_{ij}(\mathbf{R})$ is very large. We set $h_{ij}(\mathbf{R})$ equal to the product of the probability that the segments occupy a common volume multiplied by the value of the repulsive energy in the condition of segmental overlap. Thus

$$h_{ij}(\mathbf{R}) = \epsilon f(|\mathbf{r}_{ij}| < a; \mathbf{R}) \tag{3}$$

ϵ is the repulsive energy and $f(|\mathbf{r}_{ij}| < a;\mathbf{R})$ is the overlap probability. a is a mean radius of segmental overlap. The requirement that $f(|\mathbf{r}_{ij}| < a;\mathbf{R})$ be calculated as a function of $\mathbf{R}$ meets the Reiss[4] criticism of the original Edwards[3] analysis.

If $P_i(\mathbf{r}_i{\cdot}\mathbf{R})$ is the probability that monomer unit i is at $\mathbf{r}_i$ if the chain ends are at $\mathbf{O}$ and $\mathbf{R}$, and $P_j(\mathbf{r}_j;\mathbf{R})$ is similarly defined for monomer unit j

$$h_{ij}(\mathbf{R}) = \epsilon \int P_i(\mathbf{r}_i;\mathbf{R})P_j(\mathbf{r}_j;\mathbf{R})\delta(\mathbf{r}_i - \mathbf{r}_j)\, \mathrm{d}\mathbf{r}_i\, \mathrm{d}\mathbf{r}_j \tag{4a}$$

$$h_{ij}(\mathbf{R}) = \epsilon \int P_i(\mathbf{r};\mathbf{R})P_j(\mathbf{r};\mathbf{R})\, \mathrm{d}\mathbf{r} \tag{4b}$$

In the absence of excluded volume $P_i(\mathbf{r};\mathbf{R})$ and $P_j(\mathbf{r};\mathbf{R})$ are bivariate Gaussian functions. We assume that $P_i(\mathbf{r};\mathbf{R})$ and $P_j(\mathbf{r};\mathbf{R})$ are still Gaussian, but modified by a parameter, as yet unknown, such that $\langle\mathbf{R}^2\rangle$ and $\langle\mathbf{R}^{2n}\rangle$ have the correct dependence on molecular weight.

$$P_i(\mathbf{r};\mathbf{R}) = C_{\mathrm{i}} \exp[-\zeta r^2/Ki^{2\nu} - \zeta(\mathbf{R} - \mathbf{r})^2/(K(N - i)^{2\nu})] \tag{5}$$

C_i is a normalization constant which is a function of $\mathbf{R}$, $\zeta = 3/2b^2$, K is a constant which is equal to unity in the absence of excluded volume, and $\nu = 0.5$ in the absence of excluded volume. The objective of this paper is to determine ν in the presence of a substantial excluded volume effect. $P_j(\mathbf{r};\mathbf{R})$ is given by an equation such as eq 5 with j substituted for i.

It is important to recognize that the use of eq 5 in eq 1 will not lead to a correct determination of $P(\mathbf{R})$, because of the limitations of the functional form of eq 5. By contrast, the dependence of the moments $\langle\mathbf{R}^{2n}\rangle$ on molecular weight is still obtainable by a judicious choice of ν.

The next steps are routine but tedious. Equations 1b, 2, 3, 4b, and 5 are substituted in eq 1a. For the purpose of reducing the onerous details, we define the reduced variables $u = i/N$ and $v = j/N$. The sum $\sum_{i,j=1}^{N}$ of eq 2 is then replaced by $N^2\int_0^1\int_0^1 \mathrm{d}u\, \mathrm{d}v$. Carrying out the integral over $\mathbf{r}$, in eq(4b), one obtains

$$P(\mathbf{R}) = \frac{1}{Z} \exp\left[-\frac{\zeta R^2}{N} + \frac{\epsilon N^{2-3\nu}}{2kT}\varphi(R^2;N) \right] \tag{6a}$$

$$\varphi(R^2;N) = \int_0^1\int_0^1 \left(\frac{\zeta f(u,v)}{K\pi} \right)^{3/2} \exp\left[\frac{-\zeta f(u,v)g(u,v)R^2}{KN^{2\nu}} \right] \mathrm{d}u\, \mathrm{d}v \tag{6b}$$

$$f(u,v) = \frac{[(1 - u)^{2\nu} + u^{2\nu}][(1 - v)^{2\nu} + v^{2\nu}]}{[(1 - u)^{2\nu} + u^{2\nu}]v^{2\nu}(1 - v)^{2\nu} + [(1 - v)^{2\nu} + v^{2\nu}]u^{2\nu}(1 - u)^{2\nu}} \tag{6c}$$

$$g(u,v) = \left[\frac{u^{2\nu}}{(1 - u)^{2\nu} + u^{2\nu}} + \frac{v^{2\nu}}{(1 - v)^{2\nu} + v^{2\nu}} \right]^2 \tag{6d}$$

The most probable value of R^2, designated as R_{p}^2, is proportional to $N^{2\nu}$ as is $\langle R^2\rangle$. R_{p}^2 is formed from eq 6a by setting $\mathrm{d}[P(\mathbf{R})/\mathrm{d}(R^2)] = 0$. The result is

$$\psi_{\mathrm{p}} = \frac{2kTKN^{5\nu-3}}{\epsilon} \tag{7a}$$

where ψ_{p} is defined by

$$\psi_{\mathrm{p}} = \int_0^1\int_0^1 \left(\frac{\zeta}{K\pi} \right)^{3/2} (f(u,v))^{5/2}g(u,v) \times \exp[-\zeta f(u,v)g(u,v)K_{\mathrm{p}}/K]\, \mathrm{d}u\, \mathrm{d}v \tag{7b}$$

where $K_{\mathrm{p}} = R_{\mathrm{p}}^2/N^{2\nu}$. It is clear from eq 7b that ψ_{p} is independent of N. Therefore, it follows from eq 7a that $\nu = 0.6$.

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This result reproduces that of Flory, Edwards, and others. It is not a self-consistent field calculation of $P(\mathbf{R})$. However, the dependence of R^2 on N is obtained directly, independent of the correctness or incorrectness of $P(\mathbf{R})$.

References and Notes

(1) A survey of much of the literature on this subject may be found in H. Yamakawa, "Modern Theory of Polymer Solutions", Harper and Row, New York, N.Y., 1971, Chapter III.
(2) P. J. Flory, *J. Chem. Phys.*, **17**, 303 (1949).
(3) S. F. Edwards, *Proc. Phys. Soc.*, **85**, 613 (1965).
(4) H. Reiss, *J. Chem. Phys.* **47**, 186 (1967).
(5) P. G. de Gennes, *Phys. Lett. A*, **38**, 339 (1972).
(6) J. des Cloizeaux, *Phys. Rev. A*, **10**, 1665 (1974).
(7) K. J. Freed, *Adv. Chem. Phys.*, **22**, 1 (1972).
(8) F. T. Wall and J. J. Erpenbeck, *J. Chem. Phys.*, **30**, 634 (1959).
(9) C. Domb, *Adv. Chem. Phys.*, **15**, 229 (1969).

Effect of Nonrandom Mixing on Flory's Equation of State

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Renuncio and Prausnitz[1] have proposed a *one-fluid* theory, coupled with the assumption of nonrandom mixing, to obtain an equation of state from which to calculate residual thermodynamic functions. For a binary mixture, following Abrams,[2] they propose to relate local site fractions θ_{ij} to the overall site fractions θ_i and θ_j by

$$\theta_{11} = \frac{\theta_1}{\theta_1 + \theta_2\tau_{21}} \qquad \theta_{21} = \frac{\theta_2\tau_{21}}{\theta_1 + \theta_2\tau_{21}}$$
$$\theta_{22} = \frac{\theta_2}{\theta_2 + \theta_1\tau_{12}} \qquad \theta_{12} = \frac{\theta_1\tau_{12}}{\theta_2 + \theta_1\tau_{12}} \tag{1}$$

where, to simplify notation,

$$\tau_{21} = \exp(-\nu_{21}\mathbf{v}^*/RT\tilde{\mathbf{v}}) \tag{2}$$

and

$$\tau_{12} = \exp(-\nu_{12}\mathbf{v}^*/RT\tilde{\mathbf{v}}) \tag{3}$$

For the two adjustable parameters, ν_{21} and ν_{12}, the authors write

$$\nu_{21} = \frac{zq_1(\eta_{21} - \eta_{11})}{2r_1\mathbf{v}^{*2}} \qquad \nu_{12} = \frac{zq_2(\eta_{12} - \eta_{22})}{2r_2\mathbf{v}^{*2}} \tag{4}$$

As defined, the four *average* local site fractions are subjected only to the conditions

$$\theta_{11} + \theta_{21} = 1 \tag{5}$$

and

$$\theta_{22} + \theta_{12} = 1 \tag{6}$$

but, as clearly stated by Guggenheim[3] and by Hildebrand and Scott[4] in terms of distribution functions, another restraint, consistent with *one-fluid* theory, must be satisfied by local site fractions:

$$\theta_1\theta_{21} = \theta_2\theta_{12} \tag{7}$$

Equation 7 is merely a contact balance which is not verified, as Renuncio and Prausnitz have pointed out.

Therefore, Renuncio and Prausnitz have, in effect, used a *two-fluid* theory.

$$q_1N_1\theta_{21}\eta_{21} = q_2N_2\theta_{12}\eta_{12} \tag{8}$$

If they had used a *one-fluid* theory, the average energy balance of the 1–2 interactions for all values of N_1 and N_2 and for $\eta_{21} = \eta_{12}$ should have been satisfied, because of eq 7.

Further, Renuncio and Prausnitz state that the residual entropy is affected by nonrandomness, since the local compositions are temperature dependent. But why, one asks, do they use, in Appendix B, Flory's expression[5] of the residual entropy to calculate the residual chemical potential? Flory, in fact, has obtained his expression for a perfectly random mixture.

Furthermore, it is possible to demonstrate that the expression (eq B3) given by the authors for the residual enthalpy is not consistent with the expression (eq B2) for the integral heat of mixing at infinite dilution. In fact, from the definition

$$B = \frac{V_1^*}{V_2^*}\lim_{N_2\to 0}\frac{\Delta H^{\mathrm{M}}}{N_2} \tag{9}$$

applying L'Hopital's theorem, one has

$$B = \frac{V_1^*}{V_2^*}\bar{H}_2^{\mathrm{R}}(\infty) \tag{10}$$

where, from the residual enthalpy equation quoted by Renuncio,

$$\bar{H}_2^{\mathrm{R}}(\infty) = \frac{V_2^*}{\tilde{\mathbf{v}}_1}\left\{P_2^*\left(\frac{\tilde{\mathbf{v}}_1}{\tilde{\mathbf{v}}_2} - 1\right) - \left(\nu_{12} + \nu_{21}\frac{q_2/r_2}{q_1/r_1}\tau_{21}\right)\right\} \tag{11}$$

Substitution of eq 11 in eq 10 gives

$$B = \frac{V_1^*}{\tilde{\mathbf{v}}_1}\left\{P_2^*\left(\frac{\tilde{\mathbf{v}}_1}{\mathbf{v}_2} - 1\right) - \left(\nu_{12} + \nu_{21}\frac{q_2/r_2}{q_1/r_1}\tau_{21}\right)\right\} \tag{12}$$

Equation 12 differs from eq B2 reported by the authors for B. I believe that this is due to the incorrect definition of the residual enthalpy given by Renuncio and Prausnitz, in fact

$$\bar{H}_1^{\mathrm{R}} = \{\partial\Delta H^{\mathrm{M}}/\partial N_1\}_{TN_2P}$$

while the authors assume (eq B3)

$$\bar{H}_1^{\mathrm{R}} = \{\partial\Delta H^{\mathrm{M}}/\partial N_1\}_{T,N_2,\tilde{\mathbf{v}}}$$

Finally, the assumption of nonrandomness also modifies the general form of Flory's equation of state for a binary mixture, that is

$$\frac{\tilde{P}\tilde{\mathbf{v}}}{\tilde{T}} = \frac{\tilde{\mathbf{v}}^{1/3}}{\tilde{\mathbf{v}}^{1/3} - 1} - \frac{1}{\tilde{\mathbf{v}}\tilde{T}} + \frac{A}{\tilde{\mathbf{v}}^2\tilde{T}^2} \tag{13}$$

where

$$A = \frac{P^*\mathbf{v}^*}{RT^*}\left\{\phi_1\theta_{11}\theta_{21}\left(\frac{\nu_{21}}{P^*}\right)^2 + \phi_2\theta_{22}\theta_{12}\left(\frac{\nu_{12}}{P^*}\right)^2\right\} \tag{14}$$

This result contrasts with Renuncio's statement that the modifications introduced to account for nonrandomness do not affect Flory's equation of state.

Equation 13 reduces to Flory's form only when the mixtures are athermal, i.e., when ν_{21} and ν_{12} are both equal to zero.

In Table I the reduced volumes, calculated by eq 13 and by eq 8 in ref 1, at two different temperatures are compared. A symmetric ($\nu_{21} = \nu_{12}$; $q_1/r_1 = q_2/r_2$) mixture, with $\phi_2 = 0.5$, is considered. Pure-component parameters employed in both equations were: $P_1^* = 150$ cal/cm^3, $T_1^* = 5000$ K, $V_1^* = 100$ cm^3/mol, $P_2^* = 100$ cal/cm^3, $T_2^* = 8000$ K. Table I shows that the contribution of the third term in the right side of eq 13 is not a negligible quantity.

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