of such β spirals to obtain a low-energy twisted filament structure.

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Conformational Entropy Effects in a Compressible Lattice Fluid Theory of Polymers

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ABSTRACT: An earlier theory of an incompressible multicomponent system consisting of both polymers and small molecules has been modified to account for free-volume effects by taking one of the small-molecule components to be vacancies. The resulting equation-of-state theory, based on the lattice fluid model, correctly accounts for conformational entropy effects, which have been neglected by Poser and Sanchez. The theory is applied to the calculation of the surface tension of pure polymer melts, and good agreement with experiment is obtained.

1. Introduction

The equation-of-state approach to the study of polymer liquids developed by Flory and co-workers[1-4] has enjoyed great success in describing the thermodynamical properties and the phase separation behavior of polymer systems. Such phenomena as the lower critical solution temperature (LCST) behavior can be understood in terms of the equation-of-state theory whereas the older Flory–Huggins theory completely fails to describe it. A more recent version of an equation-of-state theory, based on a lattice fluid model and capable of describing both the liquid and the vapor phases, has also been advanced by Sanchez and Lacombe.[5-9]

Recently, based on a functional integral approach due to Helfand,[10] we have developed a theory for an inhomogeneous incompressible liquid consisting of both polymers and small molecules.[11] In the limit of a homogeneous system, it reduces to the Flory–Huggins theory and hence suffers from the same drawbacks, although it should be noted that for many practical applications the Flory–Huggins theory is still useful, provided the interaction parameters are used in a phenomenological sense. Nonetheless it would be desirable to have a generalization of the equation-of-state theories to describe inhomogeneous systems. Such a step has been taken by Poser and Sanchez,[9,12] who use the lattice fluid model in conjunction with the theory of Cahn and Hilliard[13] to study the interfacial properties of liquids. However, in so doing, they have neglected conformational entropy effects which are important, especially when incompatible polymer blends are involved.

The purpose of this paper is to demonstrate that our formalism[11] for an incompressible multicomponent system can easily be modified to take into account free-volume effects simply by taking one of the small-molecule components to be vacancies. Then the theory yields the equation of state of the lattice fluid model, while at the same time conformational entropy effects are properly taken care of.

In section 2 we present a reformulation of our theory and derive an expression for the interfacial tension. In section 3, we obtain the equation of state and identify the various parameters used in the theory. The theory is then applied to calculate the surface tension of some polymer liquids and the results are discussed in section 4.

2. Lattice Fluid Model

As described in detail in ref 11, the partition function Z of a multicomponent fluid can be written as a functional integral over the density ρ_i and effective field ω_i of the various components; viz.

$$Z = \mathcal{N} \int \Big(\prod_i^{0} \delta\rho_i(\cdot)\delta\omega_i(\cdot)\Big) \exp(-\mathcal{F}/k_{\mathrm{B}}T) \tag{2.1}$$

Here $\mathcal{N}$ is a normalization constant and a "0" over the product or summation sign indicates that the term $i = 0$ (describing vacancies) is included in the product or sum. $\mathcal{F}$ is the functional

$$\mathcal{F}(\{\rho_i(\cdot),\omega_i(\cdot)\}) = \int \mathrm{d}^3r \left\{ f - \frac{1}{12}\sum_{ij} W_{ij}\sigma_{ij}^{2}\vec{\nabla}\rho_i(\mathbf{r})\cdot\vec{\nabla}\rho_j(\mathbf{r}) - \sum_i^{0}\rho_i(\mathbf{r})\left[\omega_i(\mathbf{r}) + \frac{k_{\mathrm{B}}T}{Z_i} \ln\left(\frac{\rho_i(\mathbf{r})Q_i}{N_i}\right)\right]\right\} \tag{2.2}$$

$$f(\{\rho_i(\mathbf{r})\}) = \frac{1}{2}\sum_{ij} W_{ij}\rho_i(\mathbf{r})\rho_j(\mathbf{r}) + k_{\mathrm{B}}T\sum_i^{0}\frac{\rho_i(\mathbf{r})}{Z_i} \ln\left(\frac{\rho_i(\mathbf{r})}{Z_i z_i e}\right) \tag{2.3}$$

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where Z_i is the degree of polymerization and N_i the total number of monomer units of component i. W_{ij} and σ_{ij} are, respectively, the interaction and range of interaction parameters. They are related to the interaction potential $U_{ij}(r)$ between monomer units of the ith and the jth components by

$$W_{ij} = \int \mathrm{d}^3r\, U_{ij}(r) \tag{2.4}$$

$$W_{ij}\sigma_{ij}^2 = \int \mathrm{d}^3r\, r^2 U_{ij}(r) \tag{2.5}$$

where the integration is restricted to the region outside the hard core. The excluded-volume effect of the hard cores is taken into account by imposing the following constraint on the densities:

$$\sum_i^{0} \rho_i(\mathbf{r})/\rho_i^* = 1 \tag{2.6}$$

where ρ_i^* is the close-packed density of component i (which is slightly larger than the density of the pure liquid).

z_i in eq 2.3 is the kinetic energy contribution of component i to the partition function while Q_i in eq 2.2 is a functional of the effective potential ω_i. For a small-molecule component s, we have

$$Q_s = \int \mathrm{d}^3r \exp[-\omega_s(\mathbf{r})/k_\mathrm{B}T] \tag{2.7}$$

while for a polymeric component p, Q_p is related to ω_p via a modified diffusion equation; viz.

$$Q_p = \int \mathrm{d}^3r\, q_p(\mathbf{r},1) \tag{2.8}$$

where $q_p(\mathbf{r},t)$ is given by

$$\frac{1}{Z_p}\frac{\partial q_p}{\partial t} = \frac{b_p^2}{6}\nabla^2 q_p - \frac{\omega_p}{k_\mathrm{B}T}q_p \tag{2.9}$$

with the initial condition

$$q_p(\mathbf{r},0) = 1 \tag{2.10}$$

Here b_p is the Kuhn statistical length of the polymer. It may also be noted that eq 2.8 reduces to eq 2.7 when $b_p = 0$ and $Z_p = 1$.

In the spirit of a lattice model, we take into account free-volume effects by considering one of the small-molecule components ($i = 0$) to be vacancies. Clearly $Z_0 = 1$ and there is no kinetic energy contribution due to the vacancies. Instead, z_0 is to be interpreted as a normalization constant determined by[11]

$$z_0^{N_0}/N_0! = 1/V_0^{N_0} \tag{2.11}$$

which gives, using Stirling's formula,

$$z_0 e = N_0/V_0 = \rho_0^* \tag{2.12}$$

Here V_0 is the total volume available to the vacancies. ρ_0^* is the "close-packed" number density of vacancies and its reciprocal $v^* = 1/\rho_0^*$ may be regarded as the size of a lattice cell. We shall have more to say about ρ_0^* in section 3, but for the moment it is sufficient to note that v^* is a parameter of the model.

The partition function eq 2.1 is now evaluated by using a saddle-point method whereby the functional $\mathcal{F}$ (eq 2.2) is minimized under the constraint eq 2.6 and the condition that the total number of particles of each component is held fixed; i.e.

$$\int \mathrm{d}^3r\, \rho_i(\mathbf{r}) = N_i \tag{2.13}$$

Introducing the Lagrange multipliers $\eta(\mathbf{r})$ and λ_i for the constraints eq 2.6 and 2.13, respectively, we minimize $\mathcal{F}$ with respect to ω_i to obtain for a small-molecule component s

$$\rho_s(\mathbf{r}) = \rho_s^* \exp[-\omega_s(\mathbf{r})/k_\mathrm{B}T] \tag{2.14}$$

and for a polymeric component p

$$\rho_p(\mathbf{r}) = \rho_p^* \int_0^1 \mathrm{d}t\, q_p(\mathbf{r},t)q_p(\mathbf{r},1-\mathrm{t}) \tag{2.15}$$

On the other hand, minimization of $\mathcal{F}$ with respect to ρ_i leads to

$$\frac{\partial f}{\partial \rho_i(\mathbf{r})} + \frac{1}{6}\sum_j W_{ij}\sigma_{ij}^2\nabla^2\rho_j(\mathbf{r}) - \left[\omega_i(\mathbf{r}) + \frac{k_\mathrm{B}T}{Z_i}\ln\left(\frac{\rho_i(\mathbf{r})}{\rho_i^*}\right)\right] + \frac{1}{\rho_i^*}\eta(\mathbf{r}) = \lambda_i \tag{2.16}$$

and the Helmholtz free energy of the system is given by

$$\begin{aligned} F &= \mathcal{F}(\min) \\ &= \int \mathrm{d}^3r \left\{ f - \frac{1}{12}\sum_{ij} W_{ij}\sigma_{ij}^2\vec{\nabla}\rho_i(\mathbf{r})\cdot\vec{\nabla}\rho_j(\mathbf{r}) - \sum_p \rho_p(\mathbf{r})\left[\omega_p(\mathbf{r}) + \frac{k_\mathrm{B}T}{Z_p}\ln\left(\frac{\rho_p(\mathbf{r})}{\rho_p^*}\right)\right]\right\} \end{aligned} \tag{2.17}$$

As discussed in ref 11, we have set $Q_i = N_i/\rho_i^*$ by absorbing a constant into λ_i.

Equation 2.14 shows that the term in the square brackets in eq 2.16 vanishes identically for small molecules. The term also vanishes for polymeric components as well but only in regions where the system is homogeneous. For $i = 0$, we have

$$\frac{\partial f}{\partial \rho_0(\mathbf{r})} + \frac{1}{\rho_0^*}\eta(\mathbf{r}) = \lambda_0 \tag{2.18}$$

so that for $i \neq 0$

$$\frac{\partial f}{\partial \rho_i(\mathbf{r})} - \frac{\rho_0^*}{\rho_i^*}\frac{\partial f}{\partial \rho_0(\mathbf{r})} + \frac{1}{6}\sum_j W_{ij}\sigma_{ij}^2\nabla^2\rho_j(\mathbf{r}) - \left[\omega_i(r) + \frac{k_\mathrm{B}T}{Z_i}\ln\left(\frac{\rho_i(\mathbf{r})}{\rho_i^*}\right)\right] = \mu_i \tag{2.19}$$

where

$$\mu_i \equiv \lambda_i - \rho_0^*\lambda_0/\rho_i^* \tag{2.20}$$

Although defined in terms of the Lagrange multipliers here, μ_i is in fact the chemical potential of the component i in the system, thus justifying the use of the symbol. To see this, we note that in any bulk homogeneous system, the Helmholtz free energy (eq 2.17) reduces to

$$F = Vf \tag{2.21}$$

where V is the volume of the system. Hence the chemical potential of component i in a bulk phase b is given by

$$\mu_i^\mathrm{b} = \left(\frac{\partial F}{\partial N_i}\right)_{T,N',V} = \left[\frac{\partial f}{\partial \rho_i} - \frac{\rho_0^*}{\rho_i^*}\frac{\partial f}{\partial \rho_0}\right]_\mathrm{b} \tag{2.22}$$

where N' indicates that all the N_j are kept constant except N_i and N_0. From eq 2.20 it is then clear that

$$\mu_i^\mathrm{b} = \mu_i \tag{2.23}$$

for any bulk phase b, and eq 2.19 simply expresses the fact that the chemical potential of any component i is spatially constant.

Equations 2.9, 2.15, and 2.19 determine the density profiles $\rho_s(\mathbf{r})$ and $\rho_p(\mathbf{r})$ of the inhomogeneous system, and the Helmholtz free energy is then given by eq 2.17.

The interfacial tension γ can be obtained from the equation

$$F = \sum_i N_i\mu_i - PV + \gamma A \tag{2.24}$$

where P is the pressure and A the surface area of the interface. Hence

$$\gamma A = \int \mathrm{d}^3r \left\{ \Delta f(\mathbf{r}) - \frac{1}{12}\sum_{ij} W_{ij}\sigma_{ij}^2 \vec{\nabla}\rho_i(\mathbf{r})\cdot\vec{\nabla}\rho_j(\mathbf{r}) - \sum_p \rho_p(\mathbf{r}) \left[\omega_p(\mathbf{r}) + \frac{k_\mathrm{B}T}{Z_p} \ln\left(\frac{\rho_p(\mathbf{r})}{\rho_p^*}\right)\right]\right\} \tag{2.25}$$

where

$$\Delta f(\mathbf{r}) = f(\{\rho_i(\mathbf{r})\}) - \sum_i \rho_i(\mathbf{r})\mu_i + P \tag{2.26}$$

Note that only the polymeric components contribute to the last term of eq 2.25. This term accounts for the loss of conformational entropy of the polymer at the interface. In the absence of polymers, eq 2.25 reduces to the result of Cahn and Hilliard, valid for small molecules. It should also be noted that this conformational entropy term affects the interfacial tension in two ways. The first is of course the direct contribution of the term to the interfacial tension. Secondly, the conformational entropy modifies the density profiles and hence affects the remaining part of the integral.

Finally, we end this section by giving an alternative expression for the interfacial tension. From eq 2.19 we find

$$\sum_i \rho_i(\mathbf{r})\mu_i = \sum_i \rho_i(\mathbf{r}) \left[\frac{\partial f}{\partial \rho_i(r)} - \frac{\rho_0^*}{\rho_i^*}\frac{\partial f}{\partial \rho_0(\mathbf{r})}\right] + \frac{1}{6}\sum_{ij} W_{ij}\sigma_{ij}^2 \rho_i(\mathbf{r})\nabla^2\rho_j(\mathbf{r}) - \sum_p \rho_p(\mathbf{r})\left[\omega_p(\mathbf{r}) + \frac{k_\mathrm{B}T}{Z_p}\ln\left(\frac{\rho_p(\mathbf{r})}{\rho_p^*}\right)\right] \tag{2.27}$$

Substituting this into eq 2.26 we obtain

$$\gamma A = \int \mathrm{d}^3r \left\{ \Delta P(\mathbf{r}) + \frac{1}{12}\sum_{ij} W_{ij}\sigma_{ij}^2 \vec{\nabla}\rho_i(\mathbf{r})\cdot\vec{\nabla}\rho_j(\mathbf{r}) \right\} \tag{2.28}$$

where

$$\Delta P(\mathbf{r}) = P + f(\{\rho_i(\mathbf{r})\}) - \sum_i \rho_i(\mathbf{r}) \left[\frac{\partial f}{\partial \rho_i(\mathbf{r})} - \frac{\rho_0^*}{\rho_i^*}\frac{\partial f}{\partial \rho_0(\mathbf{r})}\right] \tag{2.29}$$

Other expressions for the interfacial tension are given in the Appendix.

3. Equation of State

To make contact with the equation-of-state theory of Sanchez and Lacombe,[5-9] we define the following quantities:

$$\epsilon_{ij}^* = -\frac{1}{2\rho_0^*} W_{ij}\rho_i^*\rho_j^* \tag{3.1}$$

$$r_i = Z_i\rho_0^*/\rho_i^* \tag{3.2}$$

$$\tilde{\rho}_i(\mathbf{r}) = \rho_i(\mathbf{r})/\rho_i^* \tag{3.3}$$

$$\tilde{\rho}(\mathbf{r}) = \sum_i \tilde{\rho}_i(\mathbf{r}) \tag{3.4}$$

$$u_i = Z_i z_i e/\rho_i^* \tag{3.5}$$

Then, for a homogeneous system, the Helmholtz free energy per unit volume is given by

$$f = \rho_0^*\left\{ -\sum_{ij}\epsilon_{ij}^*\tilde{\rho}_i\tilde{\rho}_j + k_\mathrm{B}T\left[\sum_i \frac{\tilde{\rho}_i}{r_i}\ln\left(\frac{\tilde{\rho}_i}{u_i}\right) + (1-\tilde{\rho})\ln(1-\tilde{\rho})\right]\right\} \tag{3.6}$$

and the chemical potential of component i is

$$\mu_i = \frac{\rho_0^*}{\rho_i^*}\left\{ -2\sum_j \epsilon_{ij}^*\tilde{\rho}_j + k_\mathrm{B}T\left[\frac{1}{r_i}\ln\left(\frac{\tilde{\rho}_i}{u_i}\right) - \ln(1-\tilde{\rho}) + \frac{1}{r_i} - 1\right]\right\} \tag{3.7}$$

The Gibbs free energy per unit volume g and the pressure P are respectively given by

$$g = \sum_i \rho_i\mu_i = \rho_0^*\left\{ -2\sum_{ij}\epsilon_{ij}^*\tilde{\rho}_i\tilde{\rho}_j + k_\mathrm{B}T\left[\sum_i \frac{\tilde{\rho}_i}{r_i}\ln\left(\frac{\tilde{\rho}_i}{u_i}\right) - \tilde{\rho}\ln(1-\tilde{\rho}) + \left(\frac{1}{r} - 1\right)\tilde{\rho}\right]\right\} \tag{3.8}$$

and

$$P = g - f = -\rho_0^*\left\{ \sum_{ij}\epsilon_{ij}^*\tilde{\rho}_i\tilde{\rho}_j + k_\mathrm{B}T\left[\ln(1-\tilde{\rho}) + \left(1 - \frac{1}{r}\right)\tilde{\rho}\right]\right\} \tag{3.9}$$

where r is defined by

$$\tilde{\rho}/r = \sum_i (\tilde{\rho}_i/r_i) \tag{3.10}$$

It can be seen that the expressions for the free energies (eq 3.6 and 3.8) and the equation of state (eq 3.9) are identical with those obtained by Lacombe and Sanchez. Hence most of the thermodynamic properties of this system can be obtained directly from their work. Thus, for example, the isothermal compressibility κ and the thermal expansion coefficient α are given by[8]

$$\kappa = \frac{1}{\rho_0^*}\,\frac{1}{k_\mathrm{B}T\tilde{\rho}[\tilde{\rho}/(1-\tilde{\rho}) + 1/r] - 2\sum_{ij}\epsilon_{ij}^*\tilde{\rho}_i\tilde{\rho}_j} \tag{3.11}$$

$$\alpha = \frac{\kappa}{T}(P + \rho_0^*\sum_{ij}\epsilon_{ij}^*\tilde{\rho}_i\tilde{\rho}_j) \tag{3.12}$$

However, it should be noted that the expression for the chemical potential, eq 3.7, is somewhat different from that derived by these authors. This is due to the fact that in their work the parameter ρ_0^* is taken to be a compositional average of the corresponding parameter ρ_{0i}^* for the pure i systems. Thus, for example, in ref 6, it is assumed that

$$\rho_0^* = \frac{1}{\tilde{\rho}}\sum_i \tilde{\rho}_i\rho_{0i}^* \tag{3.13}$$

Thus defined, ρ_0^* depends on the composition of the system and hence, for an inhomogeneous mixture it becomes a function of position. This complication appears to make the present theory unwieldy. However, for most polymers, the parameters ρ_{0i}^* (corresponding to $1/v^*$ in Table I) do not vary too much, so that for practical purposes ρ_0^* may be regarded as a constant as is assumed in this paper.

Table I
Equation-of-State Parameters and End-to-End Dimensions of Some Polymers

polymer	T^*,[a] K	v^*,[a] cm³/mol	ρ_m^*,[a] gm/cm³	$10^{-4}[\langle R^2\rangle/M]^{1/2}$,[b] nm
poly(dimethylsiloxane) (PDMS)	476	13.1	1.104	670
polyethylene (PE)	649	12.7	0.904	950
polystyrene (PS)	735	17.1	1.105	650
poly(vinyl acetate) (PVAc)	590	9.64	1.283	705
poly(methyl methacrylate) (PMMA)	696	11.5	1.269	640
poly(*n*-butyl methacrylate) (PnBMA)	627	12.1	1.125	510

[a] Reference 7. [b] Reference 14.

Table II
Kuhn Length b_p, Range of Interaction σ, and Calculated Surface Thickness d

			d (Å)		
polymer	b_p, Å	σ, Å	T = 140 °C	T = 150 °C	T = 180 °C
PDMS	5.8	4.8	8.5	8.7	9.2
PE	5.0	4.8	7.1	7.2	7.5
PS	6.6	5.3	7.1	7.2	7.5
PVAc	6.5	4.4	6.7	6.8	7.1
PMMA	6.4	4.6	6.4	6.5	6.7
PnBMA	6.1	4.7	6.7	6.8	7.1

Table III
Surface Tension of Polymers

		γ, dyn/cm			
polymer		T = 140 °C[a]	T = 150 °C[b]	T = 180 °C[a]	MW
PDMS	exptl	14.0	13.6	12.1	6×10^4,[a] 10^6 [b]
	theor	14.6	14.0	12.3	∞
PE	exptl	28.8	28.1	26.5	67 000[a,b]
	exptl	30.0		27.7	∞[a]
	theor	32.4	31.6	29.3	∞
PS	exptl	32.1	30.8	29.2	44 000,[a] 93 000[b]
	theor	32.4	31.7	29.7	∞
PVAc	exptl	28.6	27.9	25.9	11 000,[a] 45 000[b]
	theor	30.7	29.9	27.3	∞
PMMA	exptl	32.0	31.2	28.9	3000[a,b]
	theor	38.0	37.1	34.6	∞
PnBMA	exptl	24.1	23.5	21.7	37 000[a,b]
	theor	28.7	27.9	25.6	∞

[a] Experimental values from ref 19. [b] Experimental values from ref 20.

Finally, a short list of equation-of-state parameters for some pure polymers, taken from ref 7, is given in Table I. These parameters (T^*, v^*, and ρ_m^*) are related to the parameters $\epsilon^* \equiv \epsilon_{pp}^*$, ρ_0^*, and ρ_p^* by

$$\epsilon^* = k_B T^* \tag{3.14}$$

$$\rho_0^* = 1/v^* \tag{3.15}$$

$$\rho_p^* = \rho_m^*/m \tag{3.16}$$

where m is the mass of a monomer unit. The subscript in ρ_m^* indicates that it is a mass density as opposed to the various ρ's in this paper, which are number densities.

Also given in Table I is the end-to-end polymer chain dimension $\langle R^2\rangle$ taken from ref 14. From these the Kuhn lengths b_p are deduced and tabulated in Table II, where the temperature dependence of b_p is neglected. The parameters shown in Table I are used to obtain the theoretical results presented in Table III.

4. Numerical Results and Discussion

In this section we apply the theory to calculate the surface tension of pure polymer melts in a parallel development to the work of Helfand and Sapse[15] on the interfacial tension between a polymer and a solvent. We consider a planar liquid surface so that as $|x| \to \infty$, $q_p(x,t)$ satisfies the boundary condition[11]

$$q_p(\pm\infty,t) = [\tilde{\rho}(\pm\infty)]^t \tag{4.1}$$

where $\tilde{\rho}(\pm\infty)$ are obtained from the equation for the chemical potential (eq 3.7) and the equation of state (eq 3.9).

For an infinite molecular weight polymer ($Z_p = \infty$), the vapor pressure vanishes, so that

$$\tilde{\rho}(\infty) = \tilde{\rho}_b \tag{4.2}$$

$$\tilde{\rho}(-\infty) = 0 \tag{4.3}$$

where the bulk density $\tilde{\rho}_b$ of the polymer is given by the nontrivial solution of eq 3.9 with $P = 0$

$$\epsilon^* \tilde{\rho}_b^2 + k_B T[\tilde{\rho}_b + \ln(1 - \tilde{\rho}_b)] = 0 \tag{4.4}$$

When $Z_p \to \infty$, the solution of eq 2.9 for $t > 0$ may be written in the separable form

$$q_p(x,t) = (\tilde{\rho}_b)^t Q_p(x) \tag{4.5}$$

where q_p satisfies the boundary condition eq 4.1 and Q_p satisfies the equation

$$0 = \frac{b_p^2}{6}\frac{d^2}{dx^2} Q_p(x) - \frac{1}{k_B T}\omega_p(x) Q_p(x) \tag{4.6}$$

with the boundary conditions

$$Q_p(\infty) = 1 \tag{4.7}$$

$$Q_p(-\infty) = 0 \tag{4.8}$$

The polymer density profile is then given by

$$\tilde{\rho}(x) = \tilde{\rho}_b (Q_p(x))^2 \tag{4.9}$$

Aside from definition of the relevant quantities, eq 4.6 to 4.8 are not required in this paper. Instead, from eq A.10 given in the Appendix, we obtain for $Z_p = \infty$ the equation

$$\Delta f(\tilde{\rho}(x)) - \frac{1}{6}\rho_0^* \epsilon^* \sigma^2 \left[\frac{d}{dx}\tilde{\rho}(x)\right]^2 - \frac{1}{6}\rho_p^* b_p^2 \tilde{\rho}_b \left[\frac{d}{dx} Q_p(x)\right]^2 = 0 \tag{4.10}$$

where from eq 2.3, 2.27, and 3.7

$$\Delta f(\tilde{\rho}) = \rho_0^* \left\{ -\epsilon^* (\tilde{\rho} - \tilde{\rho}_b)^2 + k_B T \left[(1 - \tilde{\rho}) \ln\left(\frac{1 - \tilde{\rho}}{1 - \tilde{\rho}_b}\right) + \tilde{\rho} - \tilde{\rho}_b \right] \right\} \tag{4.11}$$

Substituting eq 4.9 into eq 4.10, we obtain the density profile

$$x = \int_{\tilde{\rho}_b/2}^{\tilde{\rho}(x)} dy \left[\left(\frac{1}{6}\rho_0^* \epsilon^* \sigma^2 + \frac{1}{24y}\rho_p^* b_p^2 k_B T \right) / \Delta f(y) \right]^{1/2} \tag{4.12}$$

which is used later in eq 4.17 to calculate the surface thickness. From eq A.13 of the Appendix, with $Z_p = \infty$, we have

$$\gamma = 2\int_{-\infty}^{\infty} \mathrm{d}x\ \Delta f(\tilde{\rho}(x)) = 2\int_0^{\tilde{\rho}_\mathrm{b}} \mathrm{d}y \left[\left(\frac{1}{6}\rho_0{}^*\epsilon^*\sigma^2 + \frac{1}{24y}\rho_p{}^*b_p{}^2k_\mathrm{B}T\right)\Delta f(y)\right]^{1/2} \tag{4.13}$$

The range of interaction σ used here can be estimated as in ref 12 by taking the interaction potential to be of the form

$$U_{pp}(r) = -(\mathrm{const})/r^6 \qquad \text{for} \qquad r > v^{*1/3} \tag{4.14}$$

yielding the range parameter

$$\sigma = \sqrt{3}v^{*1/3} \tag{4.15}$$

which are given in Table II for various polymers. The results of calculations of r using eq 4.13 are discussed later.

Before proceeding further, let us point out that Helfand and Tagami[16-18] have developed a theory for compressible inhomogeneous polymer liquids by adding a phenomenological compressibility term to the Flory–Huggins free energy. The lattice fluid theory, also describing a compressible system, is more self-contained in that such quantities as the compressibility and its compositional dependence, as well as the change of volume on mixing etc., come out directly from the theory, which is also capable of describing the vapor phase. However, Helfand and Tagami[17] have made the interesting observation that an incompressible system consisting of polymers with a small amount of a small-molecule component can be treated as a compressible polymer liquid. The same viewpoint is in fact adopted in the lattice fluid model. That is, a compressible polymeric system is treated here as an "incompressible" mixture consisting of polymers and a small-molecule component (the vacancies). In view of this, it should be clear that the development in this section is completely parallel to the work of Helfand and Sapse[14] on the properties of the interface between a polymer and a solvent. Along the same vein, the calculations by us in ref 11 can also be interpreted as a study of the temperature and molecular weight dependence of the surface tension of pure polymers, provided the identification

$$\chi = \epsilon^*/k_\mathrm{B}T \tag{4.16}$$

is made.

In Table III, we list the measured surface tensions of some polymers at different temperatures along with the molecular weight of the samples used. The data are taken from ref 19 and 20. The theoretical values are calculated from eq 4.13, where the molecular weight had been assumed to be infinite. The parameters used are taken from Tables I and II. Note that no adjustable parameters are used.

It can be seen that generally good agreement is obtained between the experimental and the theoretical values, with the latter systematically higher than the former. Poser and Sanchez,[12] using the Cahn–Hilliard equation (i.e., eq 4.13 with $b_p = 0$) to calculate the surface tension, have found their theoretical values to be systematically lower than the experimental ones. Thus, in taking into account the loss of conformational entropy at the surface, we have obtained what appears to be an overcorrection to the surface tension. Nevertheless, the discrepancy can be easily ascribed to any or all of the following possible sources of errors.

A shortcoming in the theory is the treatment of the polymer as a continuous Gaussian chain and the use of a gradient expansion near the surface of the pure polymer melt where the density profile changes abruptly. Rather than plotting out the density profiles, it is more convenient to describe the surface thickness by

$$d = \frac{1}{\tilde{\rho}_\mathrm{b}}\left.\frac{\mathrm{d}x}{\mathrm{d}\tilde{\rho}}\right|_{\tilde{\rho}=\tilde{\rho}_\mathrm{b}/2} = \frac{1}{\tilde{\rho}_\mathrm{b}}\left[\left(\frac{1}{6}\rho_0{}^*\epsilon^*\sigma^2 + \frac{1}{48\tilde{\rho}_\mathrm{b}}\rho b_p{}^2k_\mathrm{B}T\right)\Big/\Delta f\left(\frac{1}{2}\tilde{\rho}_\mathrm{b}\right)\right]^{1/2} \tag{4.17}$$

These are listed in Table II, where it can be seen that d is of the same order of magnitude as b_p or σ. This clearly leads to the question of the validity of the continuum approximation. However, Helfand and Weber[21,22] have performed a numerical calculation of a polymer–solvent interface, using a discrete lattice, and showed that the continuum approximation is in fact much better than one would have expected from the above consideration. It also shows that the interfacial tension calculated with the continuum approximation tends to be systematically higher than that calculated from the discrete model,[14] with the difference decreasing with increasing temperature, as one might expect since the surface thickness increases with temperature. Such a trend is clearly seen in Table III.

Another possible source of errors is the uncertainty in the range parameter σ, eq 4.15 being only an estimate. In fact, by adjusting σ slightly, Poser and Sanchez[12] have obtained very good agreement between their calculation and the experimental values. Similarly, there is also uncertainty in the choice of b_p, for typically a range of values is tabulated for each polymer.

In view of all these uncertainties, together with a typical experimental error of a few percent in the measurement of the surface tension, the agreement between the measured and the calculated values must be considered as satisfactory, and a more detailed comparison meaningless.

Finally, it should be noted that although the conformational entropy effects calculated here constitute only a relatively small portion of the surface tension (about 5–20%), it has been shown in earlier works[16-18,23,24] that these effects are important in the study of the interface between two incompatible polymers. In dealing with such systems, the Cahn–Hilliard theory is no longer applicable and a theory such as the one developed in this paper should be used.

Appendix

For a detailed comparison with ref 11, we define

$$\frac{\mathrm{D}f}{\mathrm{D}\rho_i} \equiv \frac{\partial f}{\partial \rho_i} + \frac{1}{\rho_i{}^*}\left(f - \sum_j^0 \rho_j \frac{\partial f}{\partial \rho_j}\right) \tag{A.1}$$

Then for any bulk homogeneous phase b, we have

$$\left.\frac{\mathrm{D}f}{\mathrm{D}\rho_i}\right|_\mathrm{b} = \mu_i - \frac{1}{\rho_i{}^*}P \equiv \hat{\mu}_i \qquad (i \neq 0) \tag{A.2}$$

$$\left.\frac{\mathrm{D}f}{\mathrm{D}\rho_0}\right|_\mathrm{b} = -\frac{1}{\rho_0{}^*}P \equiv \hat{\mu}_0 \tag{A.3}$$

Equation 2.16 can now be rewritten as

$$\frac{\mathrm{D}f}{\mathrm{D}\rho_i(\mathbf{r})} + \frac{1}{6}\sum_j W_{ij}\sigma_{ij}{}^2\nabla^2\rho_j(\mathbf{r}) - \left[\omega_i(\mathbf{r}) + \frac{k_\mathrm{B}T}{Z_i}\ln\left(\frac{\rho_i(\mathbf{r})}{\rho_i{}^*}\right)\right] + \frac{1}{\rho_i{}^*}\Delta\zeta(\mathbf{r}) = \hat{\mu}_i \tag{A.4}$$

where

$$\Delta\zeta(\mathbf{r}) = \zeta(\mathbf{r}) - \zeta^{b} \tag{A.5}$$

$$\zeta(\mathbf{r}) = \eta(\mathbf{r}) - \left[f(\{\rho_i(\mathbf{r})\}) - \sum_i^{0} \rho_i(\mathbf{r}) \frac{\partial f}{\partial \rho_i(\mathbf{r})} \right] \tag{A.6}$$

It should be clear from eq A.2 to A.4 that the bulk value ζ^{b} of $\zeta(\mathbf{r})$ is independent of the choice of the bulk phase b.

Equation A.4 is identical with the corresponding equation in ref 11 and all the mathematical development in that paper can be taken over at once. Thus from eq 2.17 and A.4 we obtain[11]

$$F = \sum_i^{0} N_i \hat{\mu}_i + \gamma A \tag{A.7}$$

with the following expression for the interfacial tension:

$$\gamma A = \int \mathrm{d}^3 r \left(\frac{1}{12} \sum_{ij} W_{ij} {\sigma_{ij}}^2 \vec{\nabla} \rho_i \cdot \vec{\nabla} \rho_j - \Delta\zeta \right) \tag{A.8}$$

Furthermore, for planar interfaces, we have the relations[11]

$$\Delta\zeta + \frac{1}{12} \sum_{ij} W_{ij} {\sigma_{ij}}^2 \left(2\rho_i \frac{\mathrm{d}^2 \rho_j}{\mathrm{d}x^2} - \frac{\mathrm{d}\rho_i}{\mathrm{d}x} \frac{\mathrm{d}\rho_j}{\mathrm{d}x} \right) - \sum_p \frac{\rho_p}{Z_p} + \sum_p {\rho_p}^* \left\{ \frac{1}{Z_p} q_p(x,1) + \int_0^1 \mathrm{d}t \, \frac{{b_p}^2}{6} \left(\frac{\partial q_p}{\partial x} - q_p \frac{\partial^2 {q_p}^\dagger}{\partial x^2} \right) \right\} = 0 \tag{A.9}$$

and

$$\Delta f + \frac{1}{12} \sum_{ij} W_{ij} {\sigma_{ij}}^2 \frac{\mathrm{d}\rho_i}{\mathrm{d}x} \frac{\mathrm{d}\rho_j}{\mathrm{d}x} - \sum_p {\rho_p}^* \left\{ \frac{1}{Z_p} q_p(x,1) + \int_0^1 \mathrm{d}t \left(\frac{{b_p}^2}{6} \frac{\partial q_p}{\partial x} \frac{\partial {q_p}^\dagger}{\partial x} + \frac{1}{Z_p} q_p \frac{\partial {q_p}^\dagger}{\partial t} \right) \right\} - \sum_p \frac{\rho_p}{Z_p} \left[\ln \left(\frac{\rho_p}{{\rho_p}^*} \right) - 1 \right] = 0 \tag{A.10}$$

where

$${q_p}^\dagger(x,t) \equiv q_p(x,1-t) \tag{A.11}$$

From these we obtain the following expressions for the interfacial tension:

$$\gamma = \sum_p {\rho_p}^* \frac{{b_p}^2}{3} \int \mathrm{d}x \int_0^1 \mathrm{d}t \, \frac{\partial q_p}{\partial x} \frac{\partial {q_p}^\dagger}{\partial x} - \frac{1}{6} \sum_{ij} W_{ij} {\sigma_{ij}}^2 \int \mathrm{d}x \, \frac{\mathrm{d}\rho_i}{\mathrm{d}x} \frac{\mathrm{d}\rho_i}{\mathrm{d}x} \tag{A.12}$$

and

$$\gamma = 2 \left\{ \int \mathrm{d}x \, \Delta f - \sum_p \frac{1}{Z_p} \int \mathrm{d}x \left[\rho_p \ln \left(\frac{\rho_p}{{\rho_p}^*} \right) + {\rho_p}^* \int_0^1 \mathrm{d}t \, q_p \frac{\partial {q_p}^\dagger}{\mathrm{d}t} \right] \right\} \tag{A.13}$$

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Experimental Study of the Conformational Energy Associated with Gauche States about CH_2–CH_2 Bonds in Poly(ethylene sulfide)

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ABSTRACT: The conformational energy E_{σ_p} associated with gauche states about CH_2–CH_2 bonds in poly(ethylene sulfide) (PSE) was estimated from rotational isomeric state analysis of experimental dipole moments and their temperature coefficients corresponding to the alternating copolymer of pentamethylene sulfide and ethylene sulfide (PXS) as well as to 1,2-bis(butylthio)ethane (BBT). For both molecular chains, reasonable agreement between theoretical and experimental values of the dipole moments was found for values of E_{σ_p} lying in the range 0.4–0.7 kcal mol^{-1}. The values of E_{σ_p} thus determined are also in fair agreement with those calculated with semiempirical potential functions.

Introduction

The conformation-dependent properties of poly(ethylene sulfide) (PSE) have not been thoroughly investigated because of the intrinsic difficulties that the polymer presents; PSE is a highly crystalline polymer which melts at temperatures above 200 °C and is unstable above the melting temperature.[1] Recently, Abe[2] reported a theoretical study on the conformational properties of PSE and found that

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