vide a good model for further study of polymer liquids.

The failure of the SL equation may lie in the fact that, as mentioned in section 2, we are dealing with dense systems where the fraction of occupied sites on the lattice is close to one. In such systems the SL equation may not be an adequate description of the system. This would account for its poor performance as illustrated by the data for the polymer and subcritical fluids.

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A Modified Cell Model Equation of State for Polymer Liquids

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ABSTRACT: We describe a modified cell model description of polymer liquids. The model has the analytical simplicity of the Flory, Orwoll, and Vrij (FOV) equation of state and describes the *PVT* data more accurately than the Simha–Somcynsky (SS) equation.

Introduction

Equations of state provide us with useful descriptions of polymer liquid systems. As a minimum requirement they provide us with accurate fitting functions with which to analyze *PVT* data. They also provide us with valuable thermodynamic information and can be used to predict the properties of polymer blends and solutions. We demonstrated in a previous paper[1] that as fitting functions, those equations derived from a cell model formalism provide the most accurate descriptions of polymer *PVT* data when a wide range of pressure and temperature is considered.

In this paper we modify the cell model equation of state and demonstrate how such an equation can provide a better description of polymer liquids. This equation provides the analytical simplicity of the Flory, Orwoll, and Vrij (FOV)[2] equation of state and an accuracy, which for most polymer liquids, exceeds the Simha–Somcynsky equation. We show that a modification of the free volume term in the free energy for the cell model of polymer liquids results in these enhanced properties.

Theory

In our previous paper[1] we demonstrated that the partition function for a system of N interacting polymers, each composed of r-mers, can be written in the form

$$Z_n = Z_{\text{int}}(gv_f)^{3Ncr} \exp(-NcrE_0/kT) \qquad (1)$$

where g is the so called "communal entropy", $3c$ is the number of effective degrees of freedom per mer which is assumed to be constant, $Z_{\text{int}} = (\hbar/mkT)^{3Ncr}$ with m being the mass of a mer, v_f is the free volume term, and E_0 is the mean potential energy per mer when all mers are placed at their cell centers (one per cell). The function $E_0(R)$ is of the form

$$E_0 = (s/2)4\eta(-A(\sigma/R)^6 + B(\sigma/R)^{12}) \qquad (2)$$

where R is the intermer separation distance, s is the number of contacts per mer, η is the characteristic mer–mer interaction energy, σ is the value at which the 6-12 Lennard-Jones potential is zero for $A = B = 1$ and A and B are geometrical factors arising from summing the contributions from all neighboring cells for a given cell geometry.

The free volume v_f is of the form

$$v_f = \int \mathrm{d}\vec{a} \exp(E_0 - E(\vec{a}))/kT \qquad (3)$$

where $E(\vec{a})$ is the interaction energy of a mer, which is free to roam about its cell, with its neighbors confined to their cell centers, and the integral is taken over the cell volume. This can be evaluated by using (2). It was observed that the cell potential is well approximated by a square well potential.[4] Using a square well potential to evaluate (3), one obtains the following expression for v_f;

$$v_f = (v^{1/3} - v_{\text{hc}}^{1/3})^3 \qquad (4)$$

where v_{hc} is the hard-core cell volume and we have neglected a geometry-dependent numerical prefactor. The cell volume is related to the intermer separation R by the relation $v = \gamma R^3$, where γ is a numerical constant which depends on the specific cell geometry used. If σ is identified as the hard-core radius then the hard-core cell volume $v_{\text{hc}} = \gamma\sigma^3$.

Thus expressing the partition function as a function of v and using the square well approximation to evaluate v_f

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we can then compute the equation of state from the relation

$$p = kT(\mathrm{d}(\ln Z_n)/\mathrm{d}V)|_T \tag{5}$$

This results in the cell model equation of state. We have shown[1] earlier that this equation of state provides a fit to the available PVT data for polymer liquids which is close, but not superior, to the SS equation of state. We next turn our attention to ways in which to improve the cell model.

In deriving the equation of state we assumed that g, the communal entropy term, is a weak function of V. We will continue with this assumption and set g equal to a constant, i.e., $g = 1$. Second, we have used the square well approximation to evaluate υ_f. The equation of state gets contributions from $E_0(V)$ and $\upsilon_f(V)$. Both terms contain information on the repulsive interaction between mers. The numerical coefficients in the potential E_0 and the definition of the hard-core cell volume are coupled by the particular choice of the cell geometry used. Therefore, the equations of state obtained are geometry dependent. This geometry dependence results from the choice of the Lennard-Jones 6-12 potential. However, we will decouple the free volume term from the potential E_0. To do this, we rewrite υ_f in the form

$$\upsilon_f = (\upsilon^{1/3} - q(\gamma\upsilon^*)^{1/3}) \tag{6}$$

where $\upsilon^* = \sigma^3$ and q is a numerical factor. We will postulate that the value of q is the same for all polymer liquids. The rationale for this approach is a follows. The polymer mers which occupy the cells of our model are attached to at least two nearest neighbors. Therefore, the identification of the hard-core cell volume is not a trival matter. One might hope, however, that there is a unique hard-core cell volume which describes the local geometry of close-packed, flexible, polymer molecules. With this construction the onus is on us to show that there is a unique value of q which best describes the polymer liquid state.

With this ansatz for the free volume and assuming a hexagonal close-packed cell geometry ($\gamma = 1/(2)^{1/2}$), the equation of state can be derived from (6) and is of the form

$$\tilde{p}\tilde{V}/\tilde{T} = \tilde{V}^{1/3}/(\tilde{V}^{1/3} - q \times 0.8909) - 2/\tilde{T}(1.2045/\tilde{V}^2 - 1.011/\tilde{V}^4) \tag{7}$$

where $\tilde{V} = \upsilon/\upsilon^*$, $\tilde{T} = T/T^*$, and $\tilde{p} = p/p^*$. As defined in the previous paper, $T^* = (s\eta)/ck$ and $p^* = (s\eta)/\upsilon^*$. This equation is formally identical with the cell model[4] equation of state except for the introduction of the parameter q. We will require that q be the same for all polymer liquids as we do not want to add a fourth adjustable parameter to the equation. To establish that there is a unique value of q we will first treat q as an adjustable parameter and fit eq 7 to each polymer data set. In those cases where eq 7 provides a good fit to a large data set, we expect that the values of q obtained will be the same to within reasonable error. In this fashion, we will establish the correct value of q appropriate for polymer liquids.

Results

The polymers used for this study were polyethylene (PE), polystyrene (PS),[5] poly(dimethylsiloxane) (PDMS), the poly(hydroxypropyl ether of bisphenol A) (PO),[6] polypropylene (PP), poly(butyl acrylate) (PBA), and poly(vinylmethyl ether) (PVME). We performed a nonlinear least-squares fit of the equation to each data set by minimizing the quantity

$$s^2 = \sum(P_i(\text{data}) - P_i(\text{fit}))^2/(N - 3) \tag{8}$$

where N is the number of data points, P(data) is the measured pressure at a given volume and temperature, and P(fit) is the value of the pressure predicted by the above equation of state. As in the previous paper[1] the largest liquid data sets available were used. In no case did the value of s^2 approach values of the order 0.2 which is the value s^2 would have if the equation fit the data to within the experimental error. We first performed a fit to the polymer data using q as an extra adjustable parameter. The average value was then used in the equation to fit to the data for each polymer. The average value of q obtained was 1.07. In all cases the value of s^2 was found to be very sensitive to the value of q. Table I shows the results of the fit of eq 8 with this value of q for the polymer samples. Also shown for comparison are the values of s^2 for the cell model and SS equations of state for these polymers. It is clear from the table that the modified cell model equation of state provides a better fit to the data. Table II shows the values of q for the different samples which gave the optimum fit and the percentage deviations in q from its average value. The biggest deviation occurs for PDMS. In this case, we can see from Table I that none of the equations of state provide very good fits to this data set, and hence, we expect a larger error will occur in the value of q obtained.

Table I
Values of s^2 for the Cell Model, Simha–Somcynsky, and Modified Cell Model Equations of State and Reduction Parameters for the Modified Cell Model[a]

	CM	SS	MCM	P^*, MPa	V^*, cm^3/g	T^*, K
PE	1.94	1.49	0.85	563.9	1.0571	5569.3
PP	1.65	1.4	0.36	429.7	1.0698	5761.1
PS	1.64	0.97	0.51	564.6	0.8706	6705.6
PVME	2.49	2.46	1.70	603.5	0.8564	5543.5
PBA	3.5	1.66	0.96	544.5	0.8550	5653.8
PO	3.15	1.1	0.89	839.0	0.7687	6316.1
PDMS	5.66	4.67	4.71	347.6	0.8933	4630.5

[a] The vaue of $q = 1.07$ was used in the modified cell model.

Table II
Optimum Values of q and the Resulting Values of s^2 for the Various Polymer Data Sets[a]

	q	s^2	$(q - \langle q \rangle)/\langle q \rangle \times 100$
PE	1.066	0.8	−0.37
PP	1.065	0.34	−0.47
PS	1.076	0.49	+0.56
PVME	1.073	1.69	+0.28
PBA	1.082	0.6	+1.2
PO	1.083	0.81	+1.3
PDMS	1.044	3.49	−2.4

[a] The percentage deviation from the average value of q is also shown.

Conclusions

The modified equation of state provides a superior fit to polymer liquid PVT data. The introduction of the parameter q can be viewed as a correction to the hard-core volume. The value used for polymer liquids corresponds approximately to a 25% increase in the hard-core volume of the cell model. We prefer to view q as a means to decouple the model from a specific geometry. Clearly, if we choose to use a cubic lattice we can always redefine the hard-core cell volume so that we recover an optimum fit. The interesting result is the fact that there exists a single value of q which provides the optimum fit for most polymer liquids we have studied using this modified equation of state. The model has the analytical simplicity of the FOV equation and an accuracy which exceeds the SS equation. It, therefore, provides a useful means with which to study polymer liquids.

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Dynamics of Rodlike Macromolecules in Nondilute Solutions: Poly(*n*-alkyl isocyanates)

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ABSTRACT: Theories of caging of rigid rodlike molecules of length L and diameter d in semidilute solution are extended to higher concentrations. Packing considerations indicate that ordering in concentrated rigid rod systems must occur below $CL^2d = 2.26$, where C is the number concentration of rods. In addition, the concentration at which the mean square deflection of a semiflexible polymer chain is equal to the cage size is calculated in terms of the ratio of the persistence length to the contour length. These and other considerations are used to interpret a series of dynamic light scattering experiments on solutions of low molecular weight samples of poly(*n*-butyl isocyanate), poly(*n*-hexyl isocyanate), and poly(*n*-octyl isocyanate). Samples of these materials were fractionated by a recrystallization procedure that was developed to minimize complications due to the presence of water. The polymer fractions selected for study were characterized by capillary viscometry, differential refractometry, infrared and ultraviolet spectroscopy, vapor pressure measurements, and total intensity light scattering. The dynamic light scattering experiments in the semidilute region, as analyzed by the programs DISCRETE and CONTIN, usually give multimodal time correlation functions that are qualitatively interpreted in terms of caging theories and rotational–translational coupling. This coupling grows in importance in a fashion consistent with caging theories as the concentration is raised or the molecular diameter is increased. In the high CL^2d region the solutions studied form either a mesophase or a gel depending on the method of solution preparation and the molecular mobility (which depends in turn on other parameters such as the axial ratio and the flexibility).

I. Introduction

Since the seminal work of Doi and Edwards,[1-3] much work has focused on the dynamics of rigid rod and wormlike macromolecules in nondilute solutions. From a theoretical point of view, these systems provide ideal model systems for studying the interactions of polymers in solution since at a given volume fraction the rodlike shape maximizes the short-range intermolecular interactions that hinder rotational motions. Since at high volume fractions such systems often form liquid crystal phases, the factors that determine when and why such transitions occur and the behavior of the system immediately before the transition may be probed. Studies of concentration effects in such systems also provide insight into the interpretation of dynamic data from systems which cannot be studied at low concentrations such as micelles.[4] From a practical point of view, stiff rodlike macromolecules are the basis of new ultrastrong polymer materials.

Most current analyses of the dynamics of rodlike macromolecules in semidilute solution are based on the theories of Doi and Edwards[1-3] (referred to hereafter as DE). Doi and Edwards modeled the hard core interactions between perfectly rigid, thin rods in terms of the cages a collection of neighbors form around any particular rod. The cage prevents the enclosed rod from executing lateral translational motion or rotational motion outside of the cage boundaries until the rod escapes the cage or the cage dissolves by having rods diffuse along their length. This theory predicts that the rod rotational diffusion becomes highly hindered at relatively low rod concentrations and that, concurrently, the solution becomes highly viscous. This initial theory predicted a much more severe slowing down of the rotational diffusion and a much lower concentration for the onset of the slowing down than was actually observed in systems that more or less approximated rigid rod systems, but it did give a qualitatively correct description of the phenomenon.

Subsequent work has utilized the original caging assumption of the DE theory but has refined some of the details. These efforts may be classified on the basis of what aspect of the original theory they modify. These are (1) cage escape mechanisms,[5] (2) effects of the molecular flexibility that exist in even rather rigid systems,[6] and (3) recalculation of cage sizes and geometry.[7-9]

In a previous paper we showed that a more detailed description of the cage geometry expected for infinitely thin rigid rods gave a substantial improvement in the agreement between experiment and theory but was not sufficient to resolve all the major discrepancies.[9] It appears that in order to bring theory into agreement with experiment within the framework of caging theories, it is necessary to introduce refinements (1) and (2) mentioned above, although this is very difficult to do quantitatively. In section II of this paper, our earlier work on cage characterization[9] is extended to show when flexibility and finite diameter should have significant effects on rod dynamics.

In section III the characterization and the preparation of solutions for light scattering of a series of short, thin and rigid poly(*n*-alkyl isocyanates) of varying diameter are described as well as the light scattering apparatus and data

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