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Equations of State for Polymer Liquids

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ABSTRACT: There are numerous equations of state in the literature which propose to describe polymer liquids. We examine the assumptions on which these various equations are based and compare them using PVT data for a wide range of polymer data. We demonstrate that those theories based on the Lennard-Jones and Devonshire[1] cell model best describe the polymer liquid state. The simple cell model provides a tractable and analytically simple equation of state for the analysis of polymer liquids.

1. Introduction

The most widely used equations of state for polymer liquids are the Flory, Orwoll, and Vrij (FOV)[2] equation, the lattice fluid theory of Sanchez and Lacombe (SL),[3] and the Simha and Somcynsky (SS)[4] hole theory. These theories are based on quite different model assumptions and one might expect that their use in describing polymer liquids would depend strongly on how those assumptions encompass the physics of the polymer liquid state.

To gain some historical perspective into this problem we will first consider the problem of a system of N interacting spherically symmetric molecules. If we divide the system into N cells, then Kirkwood[5] demonstrated that the partition function for this system can be written in the form

$$Z_n = gZ_1 \qquad (1.1)$$

where Z_1 is the partition function for a system of N particles which are constrained to remain within their cells (one per cell). For a very dense system, a simple solid, for example, it is trivial to show that the function g is equal to 1. In the opposite extreme of a noninteracting low-density gas, one can show that g takes the value e. This prompted Kirkwood[5] and others to term the function g the "communal entropy" since it reflects changes in the extra entropy in the system as a function of the density. Thus the formalism embodied in eq 1.1 may be a useful description of a system which is close to one of the two extreme cases mentioned above. To proceed with this useful formalism we can further simplify eq 1.1 if we assume that the molecules are confined to the centers of their respective cells. With this approximation Z_n can be written in the following form

$$Z_n = (\lambda^{-3}v_f \exp(-E_0/kT))^n \qquad (1.2)$$

where $\lambda = (h^2/mkT)^{1/2}$, m is the mass of a molecule, and E_0 is the potential energy of interaction of a molecule at its origin within its cell with all the other molecules placed at the origins of their respective cells. The function v_f is given by the expression

$$v_f = \int d\vec{a} \exp[-(E(\vec{a}) - E_0)/kT] \qquad (1.3)$$

where $E(\vec{a})$ is the interaction energy of a molecule at position $\vec{a}$ within its cell, with all other molecules placed at the origins of their respective cells and the integration is over the cell volume. This construction provides the basis for a class of models which can be termed cell models.[6] The equation of state for this system can then be derived from the following relation

$$p = kT(d(\ln Z_n)/dV)|_T \qquad (1.4)$$

In a general case one would obtain contributions to the equation of state from the functions $g(V)$, $v_f(V)$, and $E(V)$. By projecting the problem on to a lattice one simplifies the evaluation of the contributions from $E(V)$ and $v_f(V)$ but one is still left with the formidable problem of evaluating the behavior of g as a function of V.

In practice g is set equal to 1 or e depending on whether or not one is dealing with a system which is dense (a dense subcritical liquid) or a system which is close to a gaslike phase (a low-density supercritical liquid). Clearly one cannot hope that an equation of state derived in this manner will describe a system over a wide range of densities.

To improve on the cell model it was proposed to introduce vacant cells into the system and in this fashion one could describe the extra entropy change in the system as a function of V and T.[6,7] The physical motivation for this idea came from the experimental X-ray evidence.[8] This indicated that density changes in dense liquids occurred with only very small changes in the mean intermolecular separation, indicating that the average coordination number was changing. This type of approach yielded equations of state which described the *PVT* properties of dense liquids more accurately but at the expense of the inclusion of an ansatz for the function $v_f(V)$.

The proposition that most of the volume change takes place by the presence of holes on a lattice has lead to the development of lattice fluid models[3] of the liquid state. In such models the symmetry of the lattices is used to aid the calculation of the partition function. The lattice size is fixed so that the changes in volume can only occur by the appearance of new holes on the lattice. With the lattice construction one can then evaluate the partition function using the powerful tools of statistical mechanics.

These different formulations may be successful over limited thermodynamic domains but cannot be expected to yield equations of state valid over the entire liquid-phase domain. The one possible exception to this last remark may occur in the case of polymer liquids. Here the liquid state is bounded above by the temperature at which the polymer degrades and below by the melting temperature (T_m) or the glass transition temperature (T_g). The temperature domain ranges between −100 and 400 °C and the thermal stability bound is always less than the critical temperature for the liquid. Therefore, we might hope that an equation of state which describes the dense liquid state may be successful over the entire liquid domain.

In the next section we will show how the ideas presented above have been adapted to treat polymer liquids. We derive the FOV equation and a simple cell model (CM) using the cell model formalism.

2. Theory

We derive the FOV and the CM equations of state using the formalism outlined above. We describe the SL lattice fluid model and the SS hole theory but we will not present here detailed derivations of these equations of state.

In the cell model, one models the polymer molecules as having two distinct sets of modes. Internal modes are those associated with internal motions of the molecules which do not contribute to the equation of state properties of the liquid. The external modes are those associated with the intermolecular interactions which will affect the PVT properties of the system. In reality there can be no clear distinction made between internal and external modes. This concept, however, which was proposed by Prigogine,[9] allows us to adapt the cell model formalism to describe polymer liquids.

If one accepts the construct of a clear separation between internal and external modes of motion, one can then divide each polymer molecule into r-mers with each mer having $3c$ degrees of freedom, where c is a constant, indicating the fact that each mer is constrained by bonds. More realistically one might expect c to be a function of the temperature T and the volume V of the system. However, choosing c to be constant, we can write the partition function for a system with N interacting polymer molecules in a completely analogous fashion to the cell model for single molecules. The partition function is of the form

$$Z_n = Z_{\text{int}}(T) Z_{\text{ext}}(T,V) \exp(-rNE_0/kT) \qquad (2.1)$$

where $Z_{\text{int}} = \lambda^{-3Ncr}$, $Z_{\text{ext}} = (gv_f)^{3Ncr}$, and E_0 is the configurational or mean potential energy per mer when all mers are at their cell centers. If we evaluate v_f, the "free volume", by replacing the exact potential with a square well approximation,[10] one obtains the following expression for Z_n

$$Z_n = Z_{\text{int}}(T)((v^{1/3} - {v_{\text{hc}}}^{1/3})g(V))^{3N}{}_{cr} \exp(-rNE_0/kT) \qquad (2.2)$$

where v_{hc} is the hard core cell volume and we have neglected constant multiplicative factors. To evaluate the equation of state from (2.2) we need to know the dependence of g and E_0 on V. As before we will set g equal to a constant arguing that over the thermodynamic range of interest to us g is a weak function of V.

We will write E_0 in the form

$$E_0 = s\eta\phi(R)/2 \qquad (2.3)$$

where s is the number of contacts per mer, η is the characteristic mer–mer interaction energy, ϕ is the interaction potential, and R is the intermer separation. The form of the potential used to derive the FOV equation is

$$\phi(R) = -2(\sigma/R)^3 \qquad (2.4)$$

For the cell model we use the 6-12 Lennord-Jones potential

$$\phi(R) = 4(-A(\sigma/R)^6 + B(\sigma/R)^{12}) \qquad (2.5)$$

where A and B are constant coefficients determined by the geometry of the cell lattice. The cell volume v is related to R via the following relationship

$$v = \gamma R^3 \qquad (2.6)$$

where γ is a geometrical factor which is determined by the cell geometry ($\gamma = 1/2^{1/2}$ for a hexagonal close packed (hcp) geometry). Using (2.6) we can relate the hard-core cell volume to σ as follows:

$$v_{\text{hc}} = \gamma\sigma^3 \equiv \gamma v^* \qquad (2.7)$$

This enables us to write the potentials (2.4) and (2.5) as functions of the cell volume v. We can then write Z_n in the following form:

$$Z_n = Z_{\text{int}}(g(v^{1/3} - (v^*\gamma)^{1/3}))^{3Nrc} \exp(-Nrc\phi(\tilde{V})/2\tilde{T}) \qquad (2.8)$$

where $\tilde{T} = T/T^*$ with $T^* = s\eta/(ck)$ and $\tilde{V} = v/v^*$. The equation of state can then be computed by using (1.4) and (2.8) to obtain

$$\tilde{P}\tilde{V}/\tilde{T} = \tilde{V}^{1/3}/(\tilde{V}^{1/3} - \gamma^{1/3}) - \tilde{V}/\tilde{T}\ \mathrm{d}/\mathrm{d}v\ (\phi(\tilde{V})) \qquad (2.9)$$

where $\tilde{P} = P/P^*$ with $P^* = ckT^*/v^*$. Using (2.4) for ϕ we obtain

$$\tilde{P}\tilde{V}/\tilde{T} = \tilde{V}^{1/3}/(\tilde{V}^{1/3} - \gamma^{1/3}) - \gamma/\tilde{T}\tilde{V} \qquad (2.10)$$

Using 2.5 we obtain[10]

$$\tilde{P}\tilde{V}/T = \tilde{V}^{1/3}/(\tilde{V}^{1/3} - 1/(2^{1/2})^{1/3}) - (2/\tilde{T}\tilde{V}^2)(A - B/\tilde{V}^2) \qquad (2.11)$$

where we have assumed a hcp geometry. To obtain the more usual form of the FOV equation from (2.10) we simply choose a simple cubic geometry, i.e., $\gamma = 1$. Choosing different geometries in the case of the FOV equation will not alter the form of the equation with suitable redefinitions of the reduction parameters. Thus by using the cell model formalism we can obtain two equations of state which differ from each other in the form of the potential ϕ used to describe the nature of the interactions in the system. We notice from the above derivation that since g is not a function of V, there is no contribution from this term to the equations of state. Thus the cases where $g = 1$ or e yield the same equations of state. In comparing the above equations we will be asking the question: which of the inter–mer potentials is appropriate for a description of the PVT properties in a given thermodynamic domain?

The lattice fluid approach to the problem is simply to lay the polymer molecules on a lattice and use the powerful tools developed for lattice models to compute the partition function for a system of N polymer molecules which share the lattice with a population of empty sites. Sanchez and Lacombe performed a steepest decent calculation to evaluate the partition function. Freed et al.[11] have used field theory methods to evaluate the partition function as a power series expansion in the fraction of sites occupied by the polymer molecule. As one might expect, the leading terms in this expansion are the same as those computed by Sanchez and Lacombe. However, the higher order terms in this expansion are not small at high densities where the fraction of occupied sites is close to one. Therefore, one should be wary of applying the SL theory to pure polymer liquids at high densities.

In the lattice fluid model the lattice size is fixed, which implies that the volume increases in this model by an increase in the number of vacant lattice sites. The increase in entropy of the system is modeled by the behavior of the density of vacant lattice sites. The equation of state derived by Sanchez and Lacombe is of the form

$$\tilde{P}\tilde{V}/\tilde{T} = -\tilde{V}[\ln (1 - 1/\tilde{V}) + (1 - 1/x_p)1/\tilde{V}] - 1/\tilde{V}\tilde{T} \qquad (2.12)$$

where x_p is the number of mers per molecule. The second term on the right-hand side of the equation results from the fact that in the lattice construction the energy of interaction is proportional to $1/V$ and in this respect it is similar to the FOV equation. The reduction parameters in (2.12), i.e., P^*, T^*, and V^*, are the same as defined previously with the exception that c is set equal to one. Thus, no recourse to the idea of a separation of internal and external modes is made.

The final equation we will consider is the hole theory due to Simha and Somcynsky (SS). This is a modification of the cell model which allows some of the cells to be vacant. The fraction of occupied sites, $y(T,V)$, becomes a new variable in the problem. In this fashion the entropy associated with the mixing of holes with occupied cells can be calculated. The function y is computed from the condition

$$\mathrm{d}/\mathrm{d}y\ (Z_n)|_{v,T} = 0 \qquad (2.13)$$

The resulting equation of state is of the form

$$\tilde{P}\tilde{V}/\tilde{T} = (y\tilde{V})^{1/3}/((y\tilde{V})^{1/3} - \gamma y) - (2y)/\tilde{T}((y\tilde{V})^2)(A - B/(y\tilde{V})^2) \qquad (2.14)$$

We notice that this model reduces to the cell model in the limit of $y = 1$. This model includes the volume dependence of the function g which appeared in the partition function (2.1). However, in allowing vacant cells one can no longer evaluate the free volume term, v_f, in a straightforward fashion. One is forced to make an ansatz for this function and in the case of the SS equation this ansatz takes the form

$$v_f = v^*[y((y\tilde{V})^{1/3} - y^{1/3}) + (1 - y)(y\tilde{V})^{1/3}]^3 \qquad (2.15)$$

It should be noted that models of this type have been most successful at describing PVT data for small molecular liquids. Finally, both the SS and SL equations of state do not strictly satisfy the principle of corresponding states. In both cases, the number of mers per chain appears explicitly in the equations of state. However, in both cases it can be shown that the equations are insensitive to this parameter in the limit of long chains.

3. Experimental Data

Fits of the various theories were made to the PVT data of several polymers. The densities of the polymers were measured at room temperature and atmospheric pressure by using an autopycnometer (Micromeritics), using approximately 8-g samples. The changes in density as a function of temperture and pressure were measured by using a PVT apparatus which has been described fully elsewhere.[12] It consists of a sample cell containing about 1–2 g of sample and mercury as a confining fluid. A flexible bellows closes off one end of the sample cell. The expansion and contraction of this bellows under temperature and pressure changes is used to calculate the volume change of the sample cell, making proper allowance for the well-known volume change of the mercury. In the isothermal mode, volume readings are obtained at fixed pressure intervals (usually 10 Mpa or about 100 kg/cm^2 apart) at a constant temperature. Following measurements along an isotherm, the temperature is changed by 8–10 °C, and the process is repeated. The absolute accuracy of the device is 1–2 × 10^{-3} cm^3/g; however, volume changes as small as 1–2 × 10^{-4} cm^3/g can be resolved. A version of this PVT apparatus is available as a complete instrument from Gnomix Research, Boulder, CO.

Table I
Values of the Goodness of Fit Parameter s^2 and the Reduction Parameters P^*, T^*, and V^* Are Given for the Polymers PS, PE, PH, and PDMO

	s^2	P^*, MPa	V^*, cm^3/g	T^*, K
PE ($0 < P < 200$ MPa, $152 < T < 262$ °C)				
SL	16.97	445.1	1.105 06	625.5
FOV	9.25	516.8	1.007 6	6821.6
CM	1.942	587.6	1.126 46	4340.9
SS	1.49	796.5	1.166 96	10207.2
PS ($0 < P < 180$ MPa, $121 < T < 320$ °C)				
SL	30.6	408.3	0.906 75	772.0
FOV	11.1	474.5	0.831 53	8104.8
CM	1.64	608.2	0.922 75	5144.5
SS	0.975	778.6	0.963 90	12381.7
PDMS ($0 < P < 200$ MPa, $30 < T < 235$ °C)				
SL	102.2	281.6	0.907 33	464.8
FOV	42.6	313.0	0.836 92	5247.9
CM	5.66	378.1	1.953 11	3671.7
SS	4.67	509.6	0.985 25	8511.8
PO ($0 < P < 180$ MPa, $87 < T < 301$ °C)				
SL	36.06	598.8	0.808 46	708.48
FOV	10.89	713.6	0.739 26	7880.8
CM	3.15	888.9	0.814 18	4822.6
SS	1.1	1135.9	0.851 44	11652.4

4. Results

We compared the four equations of state described in section 2 with the same sets of PVT data. We performed a nonlinear least-squares fit of each equation by minimizing the quantity

$$s^2 = \sum_i (P_i(\text{data}) - P_i(\text{fit}))^2/(N - 3) \qquad (4.1)$$

where N is the number of data points; P(data) is the measured pressure at a given value of (V,T) for the system, and P(fit) is the value of the pressure predicted by the relevant equation of state. In performing nonlnear least-squares regression, the quantity of most statistical significance is the regression sum of squares, s^2. For small data sets, a single isotherm, for example, the value of s^2 as computed for the different equations is on the order of 0.2. This value corresponds to errors in the volume on the order of ±1–2 × 10^{-4} cm^3/g, which is consistent with the precision of the present apparatus. For such small data sets the various equations are indistinguishable and they all provide adequate fits to the data. Therefore, to use the regression sum of squares as a means to discriminate between these theories we performed the fitting procedure to liquid data sets which encompassed the largest thermodynamic range available. Under these circumstances the value of s^2 becomes large. Since much effort has been expended to eliminate systematic errors from the experimental procedure,[12] these values of s^2 reflect the inability of the various equations to fit the data. Under these circumstances it becomes a trivial matter to compare the various equations of state by using the regression sum of squares.

The four polymers chosen were polyethylene (PE), polystyrene[13] (PS), poly(dimethylsiloxane) (PDMS), and phenoxy[13] [the poly(hydroxypropyl ether of bisphenol A)] (PO). Table I shows the results of the fitting procedure when applied to the above polymers. We see that in each case the pattern is the same in that the SS equation provides the best fit to the data with the CM equation a close second. The FOV equation provides a moderately good

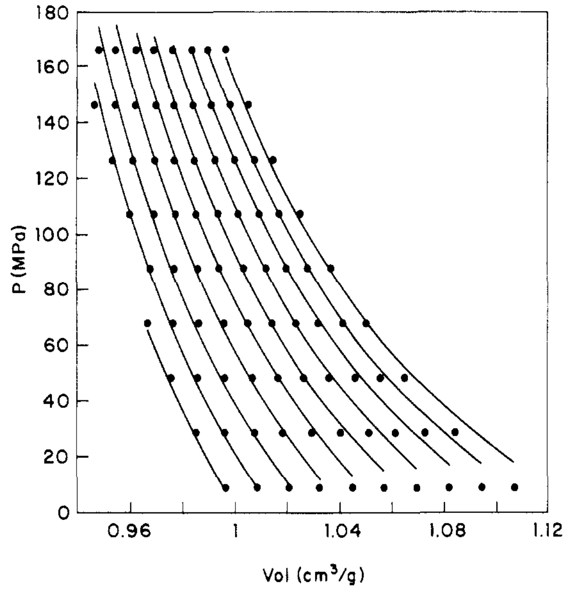

Figure 1. *PVT* data for polystyrene. The symbol ● marks the data points and the solid lines denote the best fit of the FOV equation of state to these data.

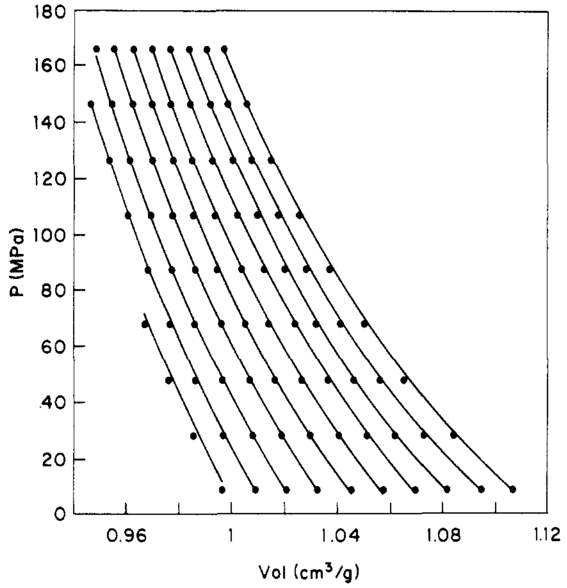

Figure 2. *PVT* data for polystyrene. The symbol ● marks the data points and the solid lines denote the best fit of the CM equation of state to these data.

fit and the SL equation provides the worst fit. The improvement in the fit between the FOV and CM equations is due to the different dependences of E_0 on the volume. We expect that in all the polymers chosen above that the dominant interactions between the polymers are of the van der Waals type. It is not too surprising, therefore, to find that the 6-12 Lennord-Jones potential provides a better description of these systems in the context of the cell model formalism.

Figure 1 shows a fit of the FOV equation to the PS data. Figure 2 shows a fit to the same data by using the CM equation. The SS equation provides a slightly better fit than does the CM equation but Figures 1 and 2 serve to illustrate the typical improvement obtained by the CM and SS equations of state over the FOV equation of state. Table I also exhibits the fact that as the thermodynamic range of the data increases, the fits of the various equations of state to the data get progressively poorer, indicating that none of the equations provide a perfect fit.

Table II
Values of the Goodness of Fit Parameter s^2 and the Reduction Parameters P^*, V^*, and T^* Are Given for Toluene and Carbon Tetrachloride

	s^2	P^*, MPa	V^*, cm^3/g	T^*, K
Toluene ($0 < P < 200$ MPa, $-50 < T < 25$ °C)				
SL	93.1	477.7	0.967 43	414.1
FOV	26.3	537.9	0.886 43	4387.8
CM	2.5	695.1	0.982 19	2761.1
SS	1.62	853.6	1.030 07	6060.8
Carbon Tetrachloride ($0 < P < 200$ MPa, $0 < T < 50$ °C)				
SL	26.2	431.0	0.5345	457.9
FOV	11.77	519.9	0.4811	4469.7
CM	0.93	614.6	0.5308	2719.9
SS	0.72	799.1	0.5540	5907.4

Table III
Values of the Goodness of Fit Parameter s^2 and the Reduction Parameters P^*, T^*, and V^* Are Given for Supercritical Freon

	s^2	P^*, MPa	V^*, cm^3/g	T^*, K
FTMC ($4 < P < 13$ MPa, $100 < T < 200$ °C)				
SL	0.044	310.1	0.5802	493.6
FOV	0.023	423.5	0.5024	4197.1
CM	2.0	173.7	0.5987	2675.4
SS	0.2	577.1	0.5380	4819.8

To obtain further insight into the possible applications of these equations of state, we compared them with *PVT* data for some typical solvents.[17] These liquids provide us with the opportunity to compare the above equations on liquids in both the supercritical and subcritical domains. The solvents chosen were toluene[14] (T), carbon tetrachloride[15] (CCl_4), and fluorotrichloromethane[16] (FTCM). Table III shows a comparison of the various equations when applied to supercritical FTCM. Table II shows the same comparison for subcritical toluene and carbon tetrachloride. In the case of the subcritical fluids we observe the same pattern as we observed for the polymers. As in the case of the polymers, the same reasons for the success of the CM equation over the FOV equation applies. In the case of the supercritical fluid we observe that the FOV equation provides the best fit to the data. The success of the FOV equation in this case is again undoubtedly due to the choice of the form of the interaction potential. The supercritical fluid is more gaslike and hence one might expect that a van der Waals potential would be more appropriate for such a fluid.

5. Conclusions

We have demonstrated that those equations of state which use the 6-12 Lennord-Jones potential to describe the interactions between the polymers, that is the CM and the SS equations of state, provide the best descriptions of the polymer liquid state. The choice of the van der Waals potential was motivated in the past by the fact that the internal energy of vaporization was found to be proportional to $1/V$ for many organic liquids. It is not surprising, therefore, to find that the FOV equation provides a good fit to a supercritical fluid. For dense subcritical liquids, however, there is no reason to expect the potential energy of interaction to scale like $1/V$. In such cases one should use the true interaction potential to determine how E_0 scales with the volume of the system.

The SS equation models the disorder in the liquid state by allowing for vacant cells. This certainly improves the fit to the PVT data but one loses the analytical simplicity of the FOV equation. The CM equation, on the other hand, provides analytical simplicity and a good description of the experimental data, and for this reason it may provide 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.

Registry No. PE, 9002-88-4; PS, 9003-53-6; FTMC, 75-69-4; PO, 25068-38-6; $C_6H_5CH_3$, 108-88-3; C, 56-23-5.

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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

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

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;

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

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 $v_{hc} = \gamma\sigma^3$.

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

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