Polymer Kirkwood Integral Equations: Structure and Equation of State of Polymeric Liquids

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A self-consistent theory of chain molecular liquids from polymer Kirkwood integral equations is presented. The theory predicts the intramolecular chain distributions and the intermolecular pair correlation functions from which thermodynamic functions can be correctly predicted. The utility of the theory is demonstrated with the chain distributions from self-consistent equations at zero density for swollen and collapsed states of the chains and numerical results for the structure and equation of state of athermal chain molecular liquids at various chain lengths and densities. Structural and thermodynamic predictions of the theory are compared with Monte Carlo simulation results. The theory agrees satisfactorily with simulation data for monomer packing fractions up to 0.25. The investigation of the chain length dependence shows that a plateau value is reached for the equation of state as the number of monomer units reaches a value between 20 and 50.

Introduction

A completely phenomenological thermodynamic treatment of long-chain molecular liquids, such as polymers, faces considerable obstacles because of the lack of constitutive equations well represented by molecular parameters for the structure and interaction. A molecular theory of such liquids can be helpful and even essential for overcoming the difficulties. The subject, however, is not as yet fully developed and constitutes an important field of study because of the practical relevance of polymeric materials. In the molecular theory of polymeric liquids statistical mechanical methods are sought after to compute the thermodynamic properties and conformations of the liquids on the basis of the interaction potentials of the subunits comprising the chain molecules.

In the Flory-Huggins theory (Flory, 1979) or its variations one approaches the problem essentially on the basis of a lattice model and mean-field treatment thereof. The theory provides qualitatively correct results for various properties of polymeric liquids, but more quantitative theories are desired. Many authors have looked for such theories. In a class of theories fashioned after the modern theory of simple liquids, the governing equations are sought after the pair correlation functions between the chain subunits or monomers in the medium of other chain molecules or simple solvent molecules. The molecular theory of chain molecular liquids which we would like to review in this article is an integral equation theory for pair correlation functions of monomer units and is capable of yielding both the structural and thermodynamic properties off the system in good accuracy.

Recent advances in computation techniques, numerical solution techniques, and speed of computation have enabled us to compute relatively easily the aforementioned properties of liquids of relatively long-chain molecules at quite modest expenses of computational effort on a commonly available workstation, thus providing a way to test molecular theories based on simple models of chain molecules in comparison with experiment or Monte Carlo simulation results. Our investigation on the dependence of the thermodynamic properties on the number of subunits indicates that the thermodynamic results for very long chain molecules can be mimicked even with chain molecules of 20-50 subunits since the plateau values are attained for thermodynamic properties as such a number of subunits is approached. The magic number for thermodynamic properties seems to lie somewhere in the neighborhood of 30 monomer units which can be comfortably handled by ordinary computing facilities. Therefore, any experimental laboratory can analyze its own thermodynamic data by means of the theory reviewed in this article.

Recent advances in the molecular theories of chain molecular liquids have employed generalizations of the liquid state theories developed for simple liquids. Schweizer and Curro (1993) adapted the reference-interaction-site-model (RISM) equation (Chandler and Anderson, 1972, 1982), which was used originally for small rigid molecules, in the context of flexible chain molecules. The polymer version of the RISM theory is nowadays called the PRISM theory. In the RISM theory, the Ornstein-Zernike equation is closed by a suitable closure assumption arrived at on diagram resummation, and the PRISM theory simply inherits such a closure relation from the RISM theory, but has also employed other closure relations in a later version of the theory (Schweizer and Yethiraj, 1993). Closure relations used in the context of the Ornstein-Zernike equation, however, is an *ad hoc* step introduced in order to break the circular relationship of direct and indirect correlation functions which is inherent to the aforementioned equation. In the case of polymers the closure relation seems to require further and closer scrutiny. One can approach the subject of correlation function theory for polymeric liquids from a different angle. The essential component of a statistical mechanics of complex liquids is various correlation functions for molecules. The governing equations for correlation functions can be derived from the first principles of statistical mechanics in the form of a hierarchy of coupled integral equations for the correlation functions (Hill, 1956). In a series of articles (Eu and Gan, 1993–1995), we have developed a generalization of the Kirkwood theory of simple liquids to the case of liquids composed of flexible chain molecules. On suitable approximations of the Kirkwood hierarchy, this theory provides a comprehensive set of governing equations for the intra- and intermolecular correlation functions in terms of which the structural and thermodynamic properties of the liquid can be expressed and computed, if the hierarchy can be suitably closed. Our studies on the properties of isolated chains (Gan and Eu, 1994) and chain molecular liquids (Gan and Eu, 1995) in comparison with Monte Carlo data suggest that this approach is computationally practicable and promising since the approximation schemes proposed capture correctly the essentials of correlations present in chain molecular liquids and their structural and thermodynamic properties.

The Kirkwood hierarchy is generated by introducing charging parameters as measures of interactions between the constituent interacting units in the system. The effects of the charging parameters are global in the sense that the interacting units get correlated regardless of their relative distance as soon as the charging parameters are turned on. Since it is important to take into account correlations over distance much longer than the interparticle interaction range, the Kirkwood charging parameter approach probably is better suited for treating the problem in hand than the kindred approach called the BGY hierarchy approach. This latter hierarchy involves partial differential equations in space. Although completely equivalent if the governing equations are solved exactly, the two approaches can give rise to somewhat different formal results if approximations are applied to them, and their numerical results can therefore differ to some extent. Attard (1995) and Taylor and Lipson (1995) have derived integral equations for the correlation functions for chain molecules based on the Born-Green-Yvon (BGY) type hierarchies. The specific approximations employed by Attard and Taylor et al. in the polymer BGY hierarchies are different from ours. The present theory also differs from the PRISM theory. A significant difference between the PRISM-type theories and the Kirkwood or BGY hierarchy is the manner in which closures are introduced to obtain approximate equations. In the Kirkwood hierarchy approach, truncation or closure of the hierarchy is effected by using some kind of superposition approximations for the triplet correlation functions on the basis of the potential elimination method. This is a method which can put the Kirkwood hierarchy in a mean-field type of equation which can be useful for developing approximate closure relations. In the BGY approach, a set of suitably modified superposition approximations is introduced so as to meet the required limiting behavior and used for the triplet correlation functions. And finally, Wertheim (1993) and others have developed the so-called thermodynamic perturbation theories for chain molecular liquids from approximate free energy functionals. In this article, we review some salient results obtained from a set of self-consistent integral equations for pair correlation functions which we have derived from the polymer Kirkwood integral equations. We present the governing equations for correlation functions which can simply be taken to compute the thermodynamic and conformational properties of polymeric liquids of interest.

Self-Consistent Integral Equations

The model for the molecule is a linear chain made up of beads or sites connected by rigid bonds with the beads acting as a universal joint. Under the assumption of pairwise additive interaction potentials, a description of the configuration distribution and thermodynamic properties of chains requires pair correlation functions obeying on the order of N^2 coupled intra- and intermolecular integral equations. Since these correlation functions are dependent on triplet and higher-order correlation functions in the exact Kirkwood hierarchy, it becomes indispensable to close the open hierarchy of the equations involved by some means. It is also helpful from the practical viewpoint in implementing numerical solutions to introduce some computation time saving stratagems. For example, as the value of N gets large, the approximate translational symmetry associated with linear chains can be exploited to reduce the set of N^2 integral equations so as to make them more readily amenable to currently available numerical solution techniques implemented on a conventional workstation. It has been argued and shown that for long linear chains the cyclic symmetry of a ring homopolymer or the translational symmetry of an infinite chain is approximately applicable (Curro and Schweizer, 1988, 1994; Gan and Eu, 1994). Cyclic symmetry implies that

$$
\begin{aligned}
h(R_{1a2q}) &= h(R), \\
\omega(R_{1p1q}) &= \omega(R_{1a,|1p-1q|}),
\end{aligned}
\tag{1}
$$

where $h(\boldsymbol{R}_{1a2q}) = g(\boldsymbol{R}_{1a2q}) - 1$ and $\omega(\boldsymbol{R}_{1p1q})$ and $g(\boldsymbol{R}_{1a2q})$ are the pair intra- and intermolecular correlation functions, respectively; the numerals 1, 2, ... are molecule indices and $a, b, \ldots, p, \ldots, N$ are site indices. By the cyclic symmetries, it is implied that the intermolecular correlation functions are independent of site indices and the intramolecular correlation functions depend only on the relative distance between beads along the chain. Under this assumption, there are $N+1$ equations to solve instead of N^2. When N is large, this approximation results in significant savings in computing requirements without incurring noticeable numerical errors in the results.

The Kirkwood hierarchy for chain molecules is led by the integral equations for intramolecular and intermolecular pair correlation functions. In these integral equations, there appear triplet correlation functions which are in turn described by integral equations involving quadruplet correlation functions and so on. The open hierarchy should be closed by some means in such a way that the closure introduced will not damage the numerical results predicted by the closed equations thus obtained. The pairwise additivity of the potential functions generally assumed indicates that the closure must be introduced in the leading pair of integral equations for intramolecular and intermolecular pair correlation functions. The potential elimination method (Eu and Gan, 1993) suggests that the lowest-order closure relation may be the Kirkwood superposition approximations for triplet correlation functions. The Kirkwood hierarchy involves an integral over the charging parameter in addition to the integrals in the configuration space. It has been shown (Eu, 1992) that the Percus-Yevick or the hypernetted chain equation for simple liquids can be obtained from the Kirkwood integral equation if the charging parameter integral is treated by approximation methods which either assume a slowly changing cavity function (for the Percus-Yevick equation) or take into account only the long range part of the cavity function (for the hypernetted chain equation). The approximate governing equations presented for the pair correlation functions of chain molecules are obtained from the polymer Kirkwood hierarchy by applying the superposition approximations and the aforementioned approximation method used for the charging parameter integral to derive the Percus-Yevick equation. The governing equations are thereby cast in the form generalizing the Percus-Yevick equation for simple liquids. Generalized hypernetted chain equations, although not presented in this article, can be also derived from the polymer Kirkwood hierarchy if the charging parameter integral is treated by the other approximation method used for the hypernetted chain equation for simple liquids. The intramolecular part of the coupled integral equations is then further simplified by applying the approximate cyclic or translational symmetry mentioned earlier. There are some more approximations of minor nature which we require to simplify the intramolecular integral equations for practical computations. Refer to Gan and Eu (1995) for the details of such approximations. With the definitions of cavity functions $y(1p2q;\ \zeta,\ \xi)$ and $y(1p1q;\ \zeta\xi)$

$$g(1p2q;\zeta,\xi)=\exp[-\xi u^*(1p2q)]y(1p2q;\zeta,\xi),$$
$$\omega(1p1q;\zeta,\xi)=\exp[-\zeta v^*(1p1q)]y(1p1q;\zeta,\xi),\qquad(2)$$

where $g(1p2q;\ \zeta,\ \xi)$ and $\omega(1p1q;\ \zeta,\ \xi)$ are the pair correlation functions of pairs $(1p2q)$ and $(1p1q)$, respectively, $u^*(1p2q)$ is the reduced potential energy defined by $u^*(1p2q)=u(1p2q)/k_BT$ for the pair $(1p2q)$, and $v^*(1p1q)$ is similarly for the pair $(1p1q)$. The symbols ζ and ξ denote the intramolecular and the intermolecular charging parameter, respectively. When these charging parameters are set equal to their full value, that is, unity, pair correlation functions and cavity functions will be written without the charging parameters explicitly written in; namely, $g(1p2q)=g(1p2q;\ \zeta=\xi=1)$, $y(1p2q)=y(1p2q;\ \zeta=\xi=1)$, and so forth. With these definitions, the governing equations for the cavity functions under the approximations mentioned earlier are

$$y(1p2q)=1+\sum_{s\neq q}^{N}\int d(2s)c(1p2s)g(2q2s)$$
$$+\rho\sum_{s\epsilon 3}^{N}\int d(3s)c(1p3s)h(2q3s),\qquad(3)$$

$$y(1p1q)=(1+\mu^*)y(1p1q;\zeta=\xi=0)$$
$$+\sum_{s\neq p,q}^{N}\int d(1s)c(1p1s)\omega(1s1q)$$
$$+\rho y(1p1q;\zeta=\xi=0)G(1p1q)$$
$$\times\sum_{s\epsilon 2}^{N}\int d(2s)c(1p2s)h(1q2s),\qquad(4)$$

where

$$\mu^*(\zeta,\xi=0)=\sum_{s\neq p}^{N}\int_0^{\zeta}d\zeta\int d(1s)v^*(1p1s)\omega(1p1s;\zeta,\xi=0)\qquad(5)$$

$$\simeq-\sum_{s\neq p}^{N}\int d(1s)c(1p1s;\zeta,\xi=0)\qquad(6)$$

with $\mu^*=\mu^*(\zeta=1,\ \xi=0)$ and

$$G(1p1q)=1-\rho\sum_{s\epsilon 2}^{N}\int d(2s)c(1p2s)h(1q2s).\qquad(7)$$

Other symbols are as follows: $c(1p2s)$, etc. are direct correlation functions defined by

$$c(1p2s;\zeta,\xi)=\{\exp[-\xi u^*(1p2s)]-1\}y(1p2s;\zeta,\xi),\text{etc.}\qquad(8)$$

and ρ is the bulk density of polymers. The symbol $d(2s)$ is an abbreviation of the volume element for monomer $2s$ in the configuration space, that is, $d(2s)=dr_{2s}$, r_{2s} being the position coordinate of $2s$. These governing equations are polymeric generalizations of the Percus-Yevick integral equations for the pair correlation function of a simple liquid. A set of generalized hypernetted chain equations can be also obtained for the polymeric liquid if the integrals involving the charging parameters are treated by a slightly different approximation. Such a derivation is described in Eu (1992) and Eu and Gan (1993). To reduce the size of a coupled set of integral equations, we apply the aforementioned translational symmetry approximation to obtain the final forms of the working equations.

Denote the Fourier transforms of indirect correlation function $h(\boldsymbol{R})$, direct correlation function $c(\boldsymbol{R})$, and so on by $\tilde{h}(\boldsymbol{k})$, $\tilde{c}(\boldsymbol{k})$, and so on. Then, the Fourier transforms of the governing integral equations given earlier can be written as

$$\tilde{h}(\boldsymbol{k}) = \frac{\tilde{\omega}(\boldsymbol{k})\tilde{c}(\boldsymbol{k})}{1 - \rho_m \tilde{c}(\boldsymbol{k})}, \tag{9}$$

$$\tilde{y}_{1a1q}(\boldsymbol{k}) = (1 + \mu^*)\tilde{\tau}(\boldsymbol{k})\omega_{1\alpha 1q}(\boldsymbol{k}) + \sum_{s \neq a,q}^{N} \tilde{c}_{1a1s}(\boldsymbol{k})[\tilde{c}_{1s1q}(\boldsymbol{k}) + \tilde{y}_{1s1q}(\boldsymbol{k})] + \rho_m \tilde{D}_{1a1q}(\boldsymbol{k}), \tag{10}$$

where $\alpha \in 1$, but $\alpha \neq a$, $\rho_m = N\rho$ is the monomer density, $\tilde{\tau}(\boldsymbol{k}) = \sin kb/kb$ incorporates the information of the fixed bond length b of the monomer, $\tilde{D}_{1a1q}(\boldsymbol{k})$ is the Fourier transform of $D_{1a1q}(\boldsymbol{R})$ defined by

$$D_{1a1q}(\boldsymbol{R}) = y_{1a1q}(\boldsymbol{R}; \zeta = \xi = 0)G_{1a1q}(\boldsymbol{R}) \times \int d\boldsymbol{R}' c(\boldsymbol{R}')h(|\boldsymbol{R} - \boldsymbol{R}'|), \tag{11}$$

and $\tilde{\omega}(\boldsymbol{k})$ is the structure function for chain configuration in the liquid defined by

$$\tilde{\omega}(\boldsymbol{k}) = \sum_{q=a}^{N} \tilde{\omega}_{1a1q}(\boldsymbol{k}). \tag{12}$$

Here $\tilde{\omega}_{1a1q}(\boldsymbol{k})$ is the Fourier transform of intramolecular correlation function $\omega(1a1q)$ and

$$y_{1a1q}(\boldsymbol{R}; \zeta = \xi = 0) \equiv y(1a1q; \zeta = \xi = 0),$$

where y_{1a1q} $(\boldsymbol{R}$; $\zeta = \xi = 0) = \tilde{\tau}(\boldsymbol{k})\omega_{1\alpha 1q}$ $(\boldsymbol{k})$. The conformation distributions of polymer chains in the medium of other polymers, such as in polymer solutions or melts, are sensitively affected by the strength of the interaction with other polymers, which is controlled by the density parameter ρ_m. Since intermolecular Eq. 9 is coupled to these intramolecular distribution functions $\tilde{\omega}_{1a1\alpha}(\boldsymbol{k})$, the governing Eqs. 9 and 10 form a set of self-consistent integral equations for intermolecular and intramolecular cavity functions or pair correlation functions. In our more recent work (Gan and Eu, 1996), it is shown that Eq. 9 represents a low-order approximation of the exact polymer Kirkwood equation for the intermolecular correlation function and it can be improved.

The indirect correlation function $h(\boldsymbol{R})$ has a range that is of the size of the polymer whereas the direct correlation function $c(\boldsymbol{R})$ has the same range as the interaction potential. It must be noted that the closure relation for $c(\boldsymbol{R})$ has the same form as the Percus-Yevick approximation (Hansen and MacDonald, 1986):

$$c(\boldsymbol{R}) = f(\boldsymbol{R})y(\boldsymbol{R})$$

where $f(\boldsymbol{R})$ is the Mayer function. For the special case of $N = 1$, we have a monatomic liquid and the structure function is given by $\tilde{\omega}(\boldsymbol{k}) = 1$. In this case, Eq. 9 reduces to the Percus-Yevick equation for a simple liquid. Therefore, Eq. 9 is a polymeric generalization of the Percus-Yevick equation for a simple liquid. To make comparison of the present theory with the PRISM theory, we list the PRISM equation

$$\tilde{h}(\boldsymbol{k}) = \tilde{\omega}_{\text{prism}}(\boldsymbol{k})^2 \tilde{c}_{\text{prism}}(\boldsymbol{k})[1 - \rho_m \tilde{\omega}_{\text{prism}}(\boldsymbol{k})\tilde{c}_{\text{prism}}(\boldsymbol{k})]^{-1}, \tag{13}$$

where c_{prism} $(\boldsymbol{R}) = f(\boldsymbol{R})y_{\text{prism}}(\boldsymbol{R})$ and $\omega_{\text{prism}}(\boldsymbol{k})$ is the Fourier transform of the intramolecular structure function. Since the PRISM theory does not have an equation for $\tilde{\omega}_{\text{prism}}(\boldsymbol{k})$, it must be provided extraneously to the theory. Therefore, the PRISM theory as expressed by Eq. 13 is not self-consistent. There are procedures developed to supply this function such as Monte Carlo simulation methods (Yethiraj and Schweizer, 1992), a variational method, (Melenkevitz et al. 1993), and so on. In any case, if $\tilde{c}(\boldsymbol{k})$ in Eq. 9 is replaced by $\tilde{\omega}_{\text{prism}}(\boldsymbol{k})\tilde{c}_{\text{prism}}$ $(\boldsymbol{k})$ the intermolecular equation in the present theory becomes the PRISM equation. The PRISM equation also reduces to the Percus-Yevick equation in the limit of $N = 1$. The present approach permits an assessment of the PRISM theory from the viewpoint of the Kirkwood integral equation. The connections between the PRISM and polymer Kirkwood integral equations are more fully explained in (Gan and Eu, 1996). Our main conclusion is that the PRISM equation is a low-order approximation of the exact polymer Kirkwood equations. The PRISM theory can be made self-consistent if $\tilde{\omega}_{\text{prism}}(\boldsymbol{k})$ and $\tilde{c}_{\text{prism}}(\boldsymbol{k})$ in Eq. 13 are replaced with $\tilde{\omega}(\boldsymbol{k})$ and $\tilde{c}(\boldsymbol{k})$, respectively, and the resulting equation is coupled to Eq. 10. Such a self-consistent PRISM theory performs better than the nonself-consistent PRISM theory as shown in Gan and Eu (1995). The molecularly based integral equation formalism presented allows us to achieve a unified description of the structure and thermodynamics of the rather complex polymeric liquids.

Equation 10 consists of three terms whose meanings are as follows. The first term on the righthand side of the equation contains the information of the chain connectivity. To see this more clearly, we take the limit $\rho_m = 0$ and turn off all monomer-monomer potentials $v_{1a1p}(\boldsymbol{R})$. In this situation, the second and third terms on the righthand side of the equation vanish and we have the result

$$\tilde{\omega}_{1a1p}(\boldsymbol{k}) = \tilde{\tau}(\boldsymbol{k})\tilde{\omega}_{1b1p}(\boldsymbol{k})(b \neq a).$$

This is a recurrence relation whose solution yields $\tilde{\omega}_{1a1p}(\boldsymbol{k}) = \tilde{\tau}(\boldsymbol{k})^{p-1}$, which is just the solution of an ideal freely jointed chain. Next, consider the situation that $\rho_m = 0$ so that the third term vanishes, but not the second term. The second term accounts for the average or mean potential of interaction between sites $1a$ and $1p$ when the potentials between the nonadjacent sites are operative. This term, of course, accounts for the excluded volume interactions. Finally, the third term on the righthand side of Eq. 10 introduces the effects of the presence of surrounding polymers on the intramolecular configuration distribution of a polymer chain. We note that the factors appearing in the expression for $D_{1a1p}(\boldsymbol{R})$ arise from the superposition approximation for a triplet correlation function. We emphasize that the intermolecular Eq. 9 is coupled to the intramolecular Eq. 10 to form a set of self-consistent equations describing chain configurations in liquids. They are solved numerically by an iterative scheme whose details are given in Gan and Eu (1994, 1995).

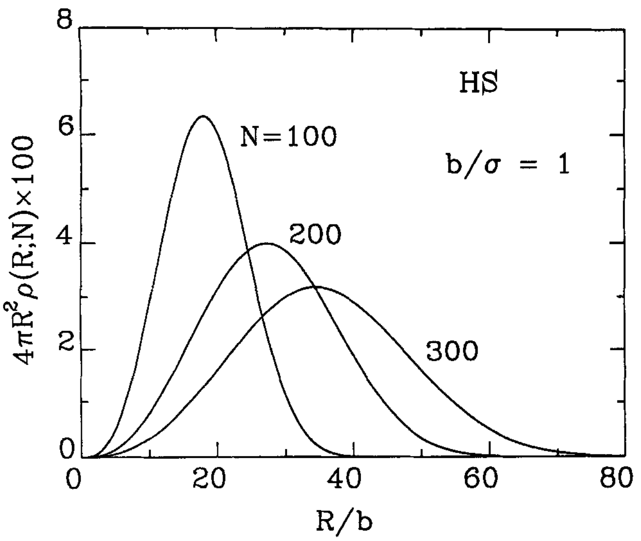

Figure 1. Monomer number distribution function of a polymer centered at one of the end beads for various values of *N*, number of bonds in the polymer chains.

Results were computed with a hard-sphere (HS) potential.

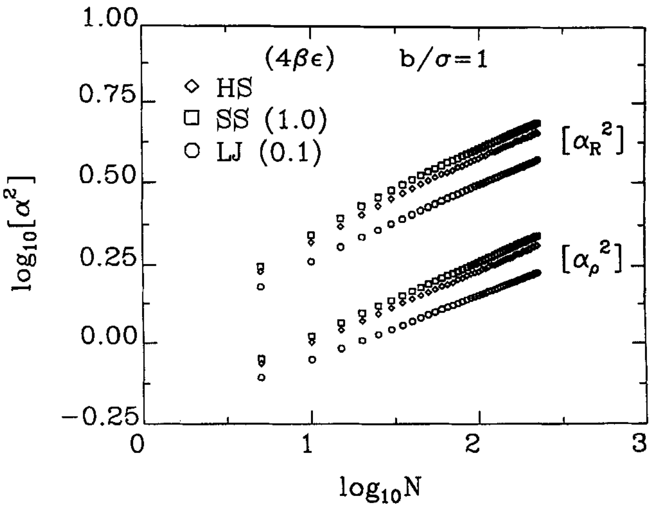

Figure 2. Expansion factors α_R^2 and α_ρ^2 as a function of *N*.

The results are obtained from Eq. 10 with three different potentials: hard-sphere (HS); soft-sphere (SS); and Lennard-Jones (LJ).

Results: Structure and Equation of State

The numerical results presented in this section are for the case of $b/\sigma = 1$. When the chain density $\rho_m = 0$ vanishes the interesting part of the self-consistent equations is the intramolecular Eq. 10. It describes the configurations of isolated chains. Figure 1 shows the density distribution function of athermal, isolated chains where the beads or sites interact by a hard-sphere potential. The bead-density distribution is broad and it indicates that the chain is swollen. In this regime, the chain statistics is determined by excluded volume interactions. We define the following second-order moments or chain expansion factors

$$\alpha_R^2(N) = \frac{1}{Nb^2}\int d^3\boldsymbol{R}R^2\omega_{1a1N}(\boldsymbol{R}), \tag{14}$$

$$\alpha^2\rho(N) = \frac{1}{(Nb)^2}\int d^3\boldsymbol{R}R^2\sum_{s=c}^{N}\omega_{1a1s}(\boldsymbol{R}). \tag{15}$$

The N dependence of the expansion factors are plotted in Figure 2 for athermal chains and also those for which the potentials of interaction are soft-sphere following the R dependence, $v = \epsilon(\sigma/R)^{12}$, and the Lennard-Jones potential $v = \epsilon[(\sigma/R)^{12} - (\sigma/R)^6]$. At high-temperature values shown, the expansion factors obey a power law of the form

$$\alpha^2(N) \propto N^{2\nu-1}.$$

From Figure 2, the exponent ν has a value of about 0.61 which is close to the Flory value of 0.6. Moreover, this value is insensitive to the nature of the potential functions used which reflects the fact that the statistics for long chains are dominated by excluded volume or hard-core interactions.

The behavior of chain molecules under theta and poor solvent conditions can be studied in the present theory by using the Lennard-Jones potential of interaction. Changes in the internal configuration distribution functions from the swollen state to the collapsed state can be monitored by varying the reduced temperature k_BT/ϵ. The size of a chain at low temperatures $k_BT/\epsilon < 1$ is less than the ideal value given by the Gaussian chain. In this regime, the single-chain integral equation predicts that the expansion factor obeys a power-law

$$\alpha_\rho^2(N) \propto |B(T) - B(\theta)|^{-\gamma}$$

where $B(T)$ is the second virial coefficient and θ is the theta temperature at which the chain distribution becomes Gaussian (Gan and Eu, 1994). The exponent γ has a value of about 0.72 for the longest chain ($N = 400$) calculated whereas de Gennes's modified Flory formula gives a value of 2/3. In the transition regime, the internal chain distribution is shown to be Gaussian at the theta temperature θ. This behavior comes about from the cancellation of the repulsive and attractive interactions which holds in the long-range part of the distribution function. The scaling properties of chain molecules emerge even when relatively short chains ($N \leq 400$) are considered. The results obtained can be extrapolated to polymers with much higher molecular weights.

Self-consistent results at finite densities are obtained by solving the coupled Eqs. 9 and 10. Figure 3 shows the intermolecular correlation function of an athermal melt where the chain length $N = 20$ and packing fraction $\eta_m = \pi N\rho\sigma^3/6 = 0.35$. The self-consistent solution agrees reasonably well with Monte Carlo data except near the contact point $R/\sigma = 1$. In contrast, the nonself-consistent result, where the intramolecular function is assumed to be an ideal Gaussian function, yields a poor agreement with data. This observation is also valid at other densities computed, but not shown here.

The virial pressure equation of state is computed by using a statistical thermodynamic formula Honnell et al. (1987)

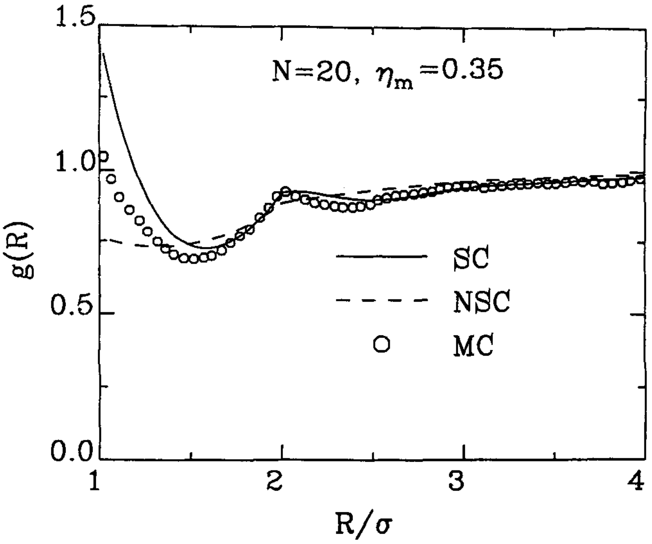

Figure 3. Intermolecular correlation function from Monte Carlo method (Yethiraj and Hall, 1992) compared with self-consistent (SC) equations nonself-consistent (NSC) result where the intramolecular function is assumed an ideal Gaussian function.

$$\frac{P}{\rho k_B T} = 1 - \frac{\rho}{6} \sum_{p,q=a}^{N} \int d^3 R R \frac{du^*(R)}{dR} g_{1p2q}(R) + \Delta_3, \quad (16)$$

where

$$\Delta_3 = -\frac{\rho}{3}(N-1)^{-1} \sum_{p\epsilon 1}^{N} \sum_{s(\neq p)\epsilon 1}^{N} \sum_{q\epsilon 2}^{N} \int d^3 R R^{-1} \frac{du^*(R)}{dR} \times \int d^3 R' \mathbf{R} \cdot \mathbf{R}' g_{1p1s2q}(\mathbf{R}, \mathbf{R}'). \quad (17)$$

Here $\mathbf{R}$ and $\mathbf{R}'$ refer to intermolecular and intramolecular vectors. Since all monomer-monomer intermolecular functions are equivalent, if the triplet correlation function is replaced by its superposition approximation, we obtain

$$\Delta_3 = -\frac{\rho_m}{3} \int d^3 \mathbf{R} R^{-1} \frac{du^*(R)}{dR} g(\mathbf{R}) J(\mathbf{R}), \quad (18)$$

where

$$J(\mathbf{R}) = \int d^3 \mathbf{R}' \mathbf{R} \cdot \mathbf{R}' G(\mathbf{R}') \omega_1(\mathbf{R}') h(|\mathbf{R} + \mathbf{R}'|) \quad (19)$$

and

$$\omega_1(\mathbf{R}') = \sum_{p=c}^{N} \omega_{1a1p}(\mathbf{R}'). \quad (20)$$

The function $J(\mathbf{R})$ can be conveniently written as convolution integrals for the purpose of numerical evaluation

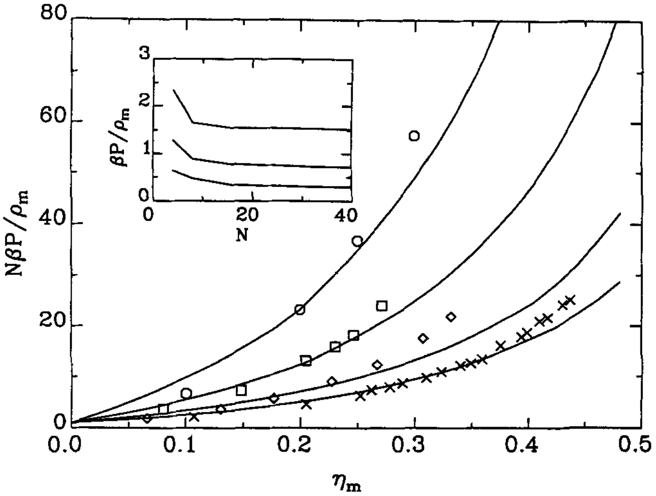

Figure 4. Virial pressure equation of state for athermal melts from self-consistent equations compared with Monte Carlo simulations of Dickman and Hall (1988) for $N=4$ (diagonal cross), 8 (diamond), 16 (square), and for 32 (octagon) from Denlinger and Hall (1990).

The chain length dependence of the factor $\beta P/\rho_m$ at three packing fractions is shown in the inset in ascending order: $\eta_m = 0.1$, 0.2 and 0.3.

$$\begin{aligned} 2J(\mathbf{R}) = & \int d^3 \mathbf{R}' |\mathbf{R} + \mathbf{R}'| G(\mathbf{R}') \omega_1(\mathbf{R}') h(|\mathbf{R} + \mathbf{R}'|) \\ & - R^2 \int d^3 \mathbf{R}' G(\mathbf{R}') \omega_1(\mathbf{R}') h(|\mathbf{R} + \mathbf{R}'|) \\ & - \int d^3 \mathbf{R}' R'^2 G(\mathbf{R}') \omega_1(\mathbf{R}') h(|\mathbf{R} + \mathbf{R}'|). \quad (21) \end{aligned}$$

We use these formulas to calculate the virial equation of state by using the solutions of the integral equations for the intramolecular and intermolecular correlation functions. Figure 4 shows a comparison of the self-consistent theory results for the equation of state with Monte Carlo data. The agreement with data holds for $N=4$ to 32 and for packing fractions at least up to 0.25. In the inset of the same figure, it is shown that the size dependence of $\beta P/\rho_m$ vanishes when $N > 20$, indicating that the thermodynamic properties for long chains can be obtained by extrapolating results computed for relatively short chains. This result is useful because self-consistent theory solutions become too time-consuming to obtain when $N > 100$, but the equation of state for a long chain molecular system can be safely obtained by considering chains of $N \geq 20$. In a further refinement of this line of theory, it is found that the contact value of the pair correlation functions and their behaviors inside the hard-core region can be dramatically improved if more careful approximate schemes are introduced into the integral equations. This result will be reported in the near future.

Concluding Remarks

We have presented coupled integral equations for intermolecular and intramolecular pair correlation functions for linear polymeric liquids. The theory gives self-consistent field equations with good numerical accuracy when the results thereof are compared with available Monte Carlo data. The numerical solutions of the self-consistent integral equations demonstrate that the structure and thermodynamics of chain molecules can be systematically investigated by means of the integral equations derived from polymer Kirkwood equations. Nevertheless, there is still room for improving the theory in a number of directions, especially, in the high packing fraction regime and numerical efficiency. To such an end, the approximations used ought to be re-examined in the light of the results already obtained. An improved superposition approximation that will not impair numerical efficiency should be desirable, but is hard to get at present by a conventional means. New improved self-consistent integral equations for intramolecular and intermolecular pair correlation functions are under study, and the numerical results obtained so far are much improved over the predictions by the present theory. The results of this study will be reported elsewhere (Gan and Eu, 1996).

Acknowledgment

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