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Importance of interactions for free-volume and end-group effects in polymers: An equilibrium lattice investigation

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We consider a lattice model of a polymer system in which we distinguish between the end (E) and the middle (M) groups. The free volume is represented as a ''hole'' or ''void'' (0), which constitutes a separate species in addition to the two ''species'' M and E. There are three different exchange interaction energies, and correspondingly three Boltzmann weights w_{ij}, $i \neq j = 0, E, M$ between different species. We define the free volume associated with the species $j = M$ or E, as the average number of voids next to j. Using a recently developed equilibrium lattice theory, we calculate the free volume v_E and v_M associated with an end group and a middle group, respectively, and investigate the effects of interactions among them. Our calculations show that v_E and v_M are intricate functions of w_{ij}, the pressure and the molecular weight, and that their difference can change sign under certain conditions. These conditions are elucidated. We demonstrate that when the end group is chemically dissimilar from the middle group, the middle group may have more free volume than the end group. We find that the conditions that favor a middle group having more free volume over an end group are $w_{E0} < 1$, $w_{M0} < 1$, and $w_{ME} > 1$. The effect of pressure and molecular weight can be of either type and appears to be dependent on the interactions.

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I. INTRODUCTION

The thermodynamic and the kinetic aspects of the liquid-glass transition provide an interesting duality, which presents one of the most challenging problems in theoretical physics [1,2]. It is fair to say that there yet exists no completely satisfying theory of the glass transition [3] even though some major progress has been made recently [4–7]. The most successful theory that attempts to describe both aspects with some respectable success is based on the ''free-volume'' model of Turnbull and Cohen [8–10]. The concept of free volume has been an intriguing one that pervades throughout physics but is not well understood [11], at least in our opinion. While the concept is intuitively appealing and very useful, it has not been put in any *quantitative* and *rational* form based on first principles. The free volume v_f associated with each molecule is, in general, different from the average volume v per molecule; the latter volume is the volume of the Voronoi cell surrounding the molecule. It should also be mentioned that the v_f is not the same as the difference $v - v_0$, where v_0 is the volume ''occupied'' by each molecule. For example, in the random close-packed state for hard spheres, it is well known that the average filling factor v_0/v is 0.637; yet, $v_f = 0$ as this is the close-packed state. Thus, one cannot identify the free volume with the empty space, unless v_0 and v are the same in the close-packed state; see, for example, Ref. [12]. (As we will see below, the latter is possible in a lattice theory.)

From the point of view of the free-volume theory, the macroscopic features are a manifestation of the redistribution of free volume at the microscopic level. In this picture, the glass transition occurs when the free volume becomes sufficiently small to impede the mobility of the molecules; this provides a *kinetic* view of the transition along with its complex time dependence. The nature of the time dependence is determined by the energy barriers encountered during redistribution, and must be properly accounted for. On the other hand, thermodynamics describes the glass transition as an equilibrium transition [1,3] in the metastable state. The investigation of this duality (equilibrium vs kinetics) is crucial for a complete understanding. Here, our aim is somewhat modest in that we deal only with equilibrium properties. In addition, we restrict our attention to temperatures well above the glass transition, as any discussion of a glass transition inevitably requires treating polymers as semiflexible and also requires considering metastable states. This adds a degree of complication that is not necessary at present if our aim is to understand the effect of energetics on the free volume. The effect of semiflexibility can easily be incorporated in our analysis [7], and will be investigated along with metastability in a separate publication.

In polymers, the problem of free volume is even more acute, as one must make a distinction between the free volume associated with the end (E) groups and with the middle (M) groups [13]. In particular, the viscosity and the glass transition temperature are dependent on the molecular weight [13,14], the latter, in turn, is related to the number of end groups. However, the energetics continues to remain unaccounted for in classical theories. End-group effects also play a major role in the overall crystallization and thickening and thinning kinetics in polymers [15]. The importance of energetics, especially due to end groups, is clearly evidenced in the behavior of surface tension. It is observed that the surface tension increases with molecular weight for the methyl-terminated polymers, decreases for the amine-terminated polymers, but is almost independent for the hydroxyl-terminated polymers [16]. The conclusion is that the methyl end groups are preferentially attracted to the surface, whereas the amine groups are depleted from the surface. A similar behavior is also observed when polybutadiene chains are end capped with two different forms of fluorosilicon groups [17]. The end-group effects are important even in the bulk where they control the phase separation behavior [18,19].

To the best of our knowledge, the above distinction between the free volumes associated with the two groups has not been formulated and investigated. We use a nearest-neighbor lattice model of the polymer system in this work, which is formally defined in the next section and allows for only nearest-neighbor interactions between different species. In this model, we define the free volume associated with the middle group (*M*) and the end group (*E*) as the average number of voids that are nearest neighbors of a middle or an end group on the lattice. Although it is a simple definition, it has the advantage that a void, which is surrounded by a wall of *E* and *M*, contributes to the free volumes associated with each of them.

One of the basic assumptions in the free-volume theory [8–10] is that the redistribution (not in time but in space) of free volume or voids occurs *randomly* and without any cost in energy [12]. While this is certainly an appealing and simplifying assumption in the model, it overlooks an important aspect of redistribution. Since a wall of molecules always surrounds each microscopic region of free volume, the interaction between molecules will certainly affect the redistribution of free volume (see below), especially when the redistribution involves free volume next to molecules. Thus, the energetics should not be ignored. Consideration of energetic effects is the central aspect of this work. Since we are not dealing with the kinetics at present, we do not concern ourselves with energy barriers encountered in the actual rearrangement of voids (in time). However, the equilibrium investigation does allow us to draw some useful conclusions about the possible kinetics. For example, it is intuitively obvious that the viscosity, a measure of the kinetics of the system, is a decreasing function of the free volume—a measure of the equilibrium property of the system: higher the free volume, easier the mobility and, hence, lower the viscosity. Thus, we can use the equilibrium study to draw conclusions about the kinetics. This is what we intend to do here.

There are two aspects of end groups that are relevant for the observed behavior. The first one is associated with the difference in the free volume of the end group and of the middle group. The other one, and which is the primary focus of our current investigation, is the influence of the energetics. The effect of energetics was recently investigated by Ryu and Gujrati [19] using a lattice theory. The model investigated was that of a polymer solution in which end groups and middle groups were treated differently. By treating the solvent species as voids, we can use this investigation to describe free volume. The investigation requires approximating the lattice by a Bethe lattice of the same coordination number *q*. It is the only approximation made. The model is solved exactly on a Bethe lattice. Because of the exact nature of the solution, thermodynamics is always obeyed. The resulting theory is a nonrandom theory and incorporates the random-mixing approximation theory (like the Flory-Huggins theory) as a limiting theory, as discussed extensively elsewhere [20].

We can use the main results of Ryu and Gujrati to study the problem of free volume associated with end and middle groups by a mere change in the ‘‘vocabulary.’’ In particular, the number N_S of solvent molecules will be replaced here by N_0, which now denotes the number of voids. Thus, the density ϕ_s of the solvent will be replaced by the density ϕ_0 of voids. Similarly, the contact density ϕ_{MS} and ϕ_{ES} between the middle groups and the solvent, and the end groups and the solvent will be replaced by ϕ_{M0} and ϕ_{E0}, respectively. Otherwise, our notation will remain unchanged. Our emphasis in the earlier publication was to investigate the effect of energetics on the phase diagram. Here, we wish to investigate the effect of the energetics on free volume associated with end and middle groups, respectively, which was not investigated by Ryu and Gujrati. We refer the reader to Ref. [19] for a complete description of thermodynamics of the model and other details that are omitted here.

The layout of the paper is as follows. We describe the original model used by Ryu and Gujrati in the next section. We change the notation, as discussed above, to suit our purpose here. We introduce the concept of the free volume associated with the two groups in Sec. III. The effect of energetics is investigated analytically and numerically in Sec. IV. In the last section, we discuss relevant experimental results and observations that highlight new results obtained in the measurement of free volume and related phenomena. We compare these results with the conclusions drawn from our analysis. This section also contains a brief summary of our results.

II. MODEL

Consider a lattice of *N* sites and of coordination number *q*. We consider a pure system consisting of linear polymers whose end groups are treated as a species different from its middle groups. Each polymer chain has exactly *b* bonds and $M=b+1$ monomers among which two monomers are end groups and others are middle groups. (The use of *M* for the number of monomers in each chain should not be confused with the subscript use of *M*, where it refers to a middle group, as in ω_{M0}.) Each monomer of the polymer occupies a site of the lattice. The remaining sites of the lattice are occupied by voids, each of which occupies only one site of the lattice. The excluded-volume effects are represented by the requirement that only one monomer can occupy a site of the lattice. The only allowed interactions are between nearest-neighbor unlike species. Let N_0, N_E, and N_M denote the number of voids, end groups, and middle groups, respectively. Then, we have

$$N_0+N_E+N_M=N. \tag{2.1}$$

In the thermodynamic limit $N\rightarrow\infty$, N_0, N_E, and N_M all diverge but the corresponding densities $\phi_0=N_0/N$, $\phi_E=N_E/N$, $\phi_M=N_M/N$ remain fixed. Thus, Eq. (2.1) can be written in terms of densities as follows:

$$\phi_0+\phi_E+\phi_M=1. \tag{2.2}$$

Let B and $N_m = N_E + N_M$ denote the total number of bonds and monomers in all polymer molecules, respectively. Then, the bond density ϕ and the monomer density $\phi_m = \phi_E + \phi_M$ are defined by the limiting values of B/N and N_m/N, $N \to \infty$, respectively. Since each polymer molecule has two end groups and $M-2$ middle groups, it is easily seen that

$$\begin{aligned} \phi_E &= (2/M)\phi_m = (2/b)\phi, \\ \phi_M &= (1-2/M)\phi_m = (1-1/b)\phi. \end{aligned} \tag{2.3}$$

Therefore, once ϕ (or ϕ_m) is given, ϕ_0, ϕ_E, and ϕ_M can be easily determined from Eqs. (2.2) and (2.3). If N_{00}, N_{E0}, and N_{M0} denote the number of void/void, end-group/void, middle-group/void pairs, respectively, and N_{EE}, N_{ME}, and N_{MM} the number of unbonded end-group/end-group, middle-group/end-group, and middle-group/middle-group pairs, respectively, then it is easy to see the following topological identities:

$$qN_0 = 2N_{00} + N_{E0} + N_{M0}, \quad qN_E = \frac{2}{b}B + 2N_{\mathrm{EE}} + N_{ME} + N_{E0},$$

$$qN_M = 2(1-1/b)B + 2N_{\mathrm{MM}} + N_{M0} + N_{ME}. \tag{2.4}$$

We now introduce densities $\phi_{ij} = N_{ij}/N$, $(i,j = 0,E,M)$ in the thermodynamic limit. In terms of densities, the above identities are given by

$$\begin{aligned} q\phi_0 &= 2\phi_{00} + \phi_{E0} + \phi_{M0}, \\ q\phi_E &= (2/b)B + 2\phi_{\mathrm{EE}} + \phi_{ME} + \phi_{E0}, \\ q\phi_M &= 2(1-1/b)B + 2\phi_{\mathrm{MM}} + \phi_{M0} + \phi_{ME}. \end{aligned} \tag{2.5}$$

Thus, among the densities ϕ_0, ϕ_E, ϕ_M, ϕ (or ϕ_m), ϕ_{00}, ϕ_{E0}, ϕ_{M0}, ϕ_{EE}, ϕ_{ME}, and ϕ_{MM} only four densities are independent due to the six constraints enforced by Eqs. (2.2), (2.3), and (2.5).

We choose ϕ, ϕ_{E0}, ϕ_{M0}, and ϕ_{ME} to be the independent densities. Let K be the activity corresponding to ϕ and let $w_{E0} = \exp(-\beta\varepsilon_{E0})$, $w_{M0} = \exp(-\beta\varepsilon_{M0})$, and $w_{ME} = \exp(-\beta\varepsilon_{ME})$ be the Boltzmann weights corresponding to the three kinds of pair densities specified by the subscripts. Here β is the inverse temperature in the unit of the Boltzmann constant. The ''exchange interaction energies'' ε_{E0}, ε_{M0}, and ε_{ME} are related to the ''direct interaction energies'' $e_{ij}, i,j = M,E,0$ in the conventional manner,

$$\varepsilon_{ij} = e_{ij} - (e_{ii} + e_{jj})/2, \quad i,j = M,E,0. \tag{2.6}$$

These simple relations between ε_{ij} and e_{ij} are due to the geometrical constraint (2.4) imposed by the homogenous lattice structure as is easily checked.

Let $X = \{B, N_{M0}, N_{E0}, N_{ME}\}$ denote the set of independent quantities. Let $\Omega(X)$ denote the number of distinct configurations of the polymer system of our interest on the lattice for a prescribed set X. The partition function Z for our model is given by

$$Z = \sum \Omega(B, N_{M0}, N_{E0}, N_{ME}) K^B w_{M0}^{N_{M0}} w_{E0}^{N_{E0}} w_{ME}^{N_{ME}}, \tag{2.7}$$

where the summation is over all possible but distinct values of quantities in the set X consistent with N. In the thermodynamic limit $N \to \infty$, the entropy per site S is given by a function of q, ϕ, ϕ_{E0}, ϕ_{M0}, and ϕ_{ME},

$$S \equiv S(q, \phi, \phi_{M0}, \phi_{E0}, \phi_{ME}) = \lim_{N \to \infty} (\ln \Omega / N), \tag{2.8}$$

such that

$$\begin{aligned} &\frac{\partial S}{\partial \phi} = -\ln K = -\beta\mu, \quad \frac{\partial S}{\partial \phi_{E0}} = -\ln w_{E0}, \\ &\frac{\partial S}{\partial \phi_{M0}} = -\ln w_{M0}, \quad \frac{\partial S}{\partial \phi_{ME}} = -\ln w_{ME} \end{aligned} \tag{2.9}$$

in equilibrium. Here μ is the chemical potential for adding a polymer bond. In the partial derivatives above, we must keep fixed all other densities in the arguments ϕ, ϕ_{E0}, ϕ_{M0}, and ϕ_{ME} of S that are not involved in differentiation. The free energy per site $\omega = \ln Z/N, N \to \infty$, is obtained from the entropy S by the following Legendre transform [19]:

$$\begin{aligned} \omega(K, w_{E0}, w_{M0}, w_{ME}) \equiv{}& S + \phi \ln K + \phi_{E0} \ln w_{E0} \\ &+ \phi_{M0} \ln w_{M0} + \phi_{ME} \ln w_{ME}, \end{aligned} \tag{2.10}$$

such that

$$\begin{aligned} &K\frac{\partial \omega}{\partial K} = \phi, \quad w_{E0}\frac{\partial \omega}{\partial w_{E0}} = \phi_{E0}, \\ &w_{M0}\frac{\partial \omega}{\partial w_{M0}} = \phi_{M0}, \quad w_{ME}\frac{\partial \omega}{\partial w_{ME}} = \phi_{ME}. \end{aligned} \tag{2.11}$$

In the partial derivatives above, we must keep fixed all other arguments K, w_{E0}, w_{M0}, and w_{ME} of ω that are not involved in differentiation.

III. FREE VOLUME ASSOCIATED WITH GROUPS

We are now set to introduce the concept of free volume associated with the two kinds of groups, M and E. We first remark that in our model, the void and each of the two groups occupy the same volume, the volume v_0 associated with each lattice site. In this picture, v_0 denotes the volume of a cell of the lattice. Such identification endows each monomer a cubical shape, which is not very realistic. Nevertheless, we will adopt this picture here. The volume v per monomer is identical to the volume v_0 in the absence of voids. In this case, the free volume v_f is identically zero and the empty space also vanishes as the filling factor is unity. Thus, in our model, the free volume and the empty space are equivalent. Of course, one can, with a slight modification, treat the volume v_m of each monomer to be different from v_0.

The amount of *total* free volume in our model is $V_f = N_0 v_0$ and the total volume $V = N v_0$. It is possible to partition equally either the total volume or the total free volume per middle group or per end group in a trivial fashion. Then, the volume per middle group or per end group would be identical. Such a partition of free volume is not consistent with the customary notion of free volume according to which end groups tend to have more free volume than middle groups [13,14]. A variety of definitions for free volume associated with a molecule or group can be found in the literature. Cohen and Turnbull [8] define the average free volume per molecule as the difference between $\overline{v}$, the average volume per molecule and $\tilde{v}_0$, its van der Waals volume. Liu, Deng, and Jean [21] note that the occupied volume $\tilde{v}_0$ has also been defined by other workers as (1) the crystalline volume at 0 K, and (2) the volume swept by the center of gravity of molecules due to fluctuations. Yet in another definition, the free volume associated with a hard sphere in a hard sphere liquid is the volume over which the center of the given sphere can translate while the other spheres are fixed; see, for example, Refs. [12], [22]. According to this view, this free volume should not be confused with the *cavity volume*, which is the volume of a continuous region of space available for inserting another sphere. In general, the above definitions relate free volume with the overall possible motion of the entity in question.

We define the free volume associated with a group in a slightly different manner. We note that, if the free volume has to play any role in the instantaneous *dynamics* of the system, it is important to consider only that part of free volume, which is *next* to monomers. This is important since the movement of a monomer at any instant can only be possible if a void is next to it; voids far away from the monomers play no appreciable role at that instant of motion. Furthermore, due to the restriction that a void occupies the same volume as a monomer, the proximity of a single void is sufficient for instantaneous or local motion. We take this viewpoint in the following, even though we are not concerned with the dynamics at present. We do so because our eventual aim is to investigate the kinetic aspect.

It is evident from the above discussion that a useful way to introduce the concept of free volume associated with any group on a lattice is to take into account the immediate presence of voids next to the group. We, therefore, identify the free volume by the close contacts N_{M0} and N_{E0}. The following quantities

$$v_M \equiv N_{M0}/N_M = \phi_{M0}/\phi_M, \tag{3.1}$$

$$v_E \equiv N_{E0}/N_E = \phi_{E0}/\phi_E, \tag{3.2}$$

determine the *average* free volume associated with a middle group and an end group, respectively. It is evident that these quantities depend on *q*, *M*, and the three interaction energies ε_{M0}, ε_{E0}, and ε_{ME}. Since voids form an ‘‘inert’’ species, it is important to take into account the fact that the ‘‘direct interaction energies’’

$$e_{00} = e_{M0} = e_{E0} = 0. \tag{3.3}$$

Hence, we observe that

$$\varepsilon_{M0} = -e_{\mathrm{MM}}/2, \quad \varepsilon_{E0} = -e_{\mathrm{EE}}/2. \tag{3.4}$$

In most cases of interest, where a pure monomeric fluid composed of M or E forms a liquid state, the van der Waals energies e_{MM} and e_{EE} are negative. (A negative value of the direct interaction energy corresponds to attractive interactions.) This implies that ε_{M0} and ε_{E0} are mostly positive; consequently, w_{M0} and w_{E0} are less than 1. On the other hand, w_{ME} can be both less than or greater than 1. However, for completeness, we will also consider w_{M0} and w_{E0} larger than 1 to allow for directional interactions.

According to Ryu and Gujrati [19], the *w*’s are related to the contact densities via

$$w_{M0} = \phi_{M0}/2\sqrt{\phi_{\mathrm{MM}}\phi_{00}}, \quad w_{E0} = \phi_{E0}/2\sqrt{\phi_{\mathrm{EE}}\phi_{00}}, \\ w_{ME} = \phi_{ME}/2\sqrt{\phi_{\mathrm{MM}}\phi_{\mathrm{EE}}}. \tag{3.5}$$

Let us introduce ϕ_{00}^0, the athermal value of ϕ_{00}, when all *w*’s are equal to 1. It is found that [19]

$$\phi_{00}^0 = \phi_{0u}^2/\phi_u, \tag{3.6}$$

where $\phi_u = q/2 - \phi$ and $\phi_{0u} = q\phi_0/2$. The adimensional pressure, as shown recently [23], is given by the adimensional pressure z_0 given in Ref. [19],

$$z_0 \equiv \beta P v_0 = -\ln \phi_0 + \frac{q}{2}\left\{\ln \frac{2\phi_u}{q} + \ln \frac{\phi_{00}^0}{\phi_{00}}\right\}. \tag{3.7}$$

Here, v_0 is the volume per site, which we will absorb in the definition of z_0.

IV. NUMERICAL RESULTS

Molecular weight has been recognized as an important parameter that dictates the thermal and mechanical properties of amorphous polymers and in particular, the glass transition temperature T_g. The common belief that the T_g must decrease with decreasing molecular weight stems from the prevalent notion of the end groups having *more* free volume than the middle groups. This gives rise to increasing free volume with decreasing molecular weight, which reduces the T_g. While this argument is certainly correct when the end groups are chemically and structurally similar to the middle groups [24], it does not take into account those polymeric systems in which the end groups may be different from the middle groups due to the method used in their synthesis or otherwise. We demonstrate that the energetics, which originates due to the dissimilarity between the end groups and middle groups, has a dramatic effect on the distribution of free volume. In particular, we identify the different factors that control this distribution and can cause the middle groups to have more free volume than the end groups. We denote the excess free volume associated with an end group over the middle group by

$$v_{\mathrm{ex}} = v_E - v_M.$$

Thus, when v_{ex} is positive, the end group has more free volume than a middle group and vice versa.

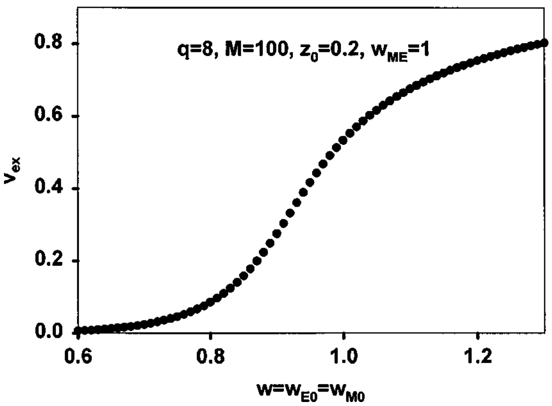

FIG. 1. v_{ex} as a function of w for a system in which the end groups and middle groups are treated similar. As w is increased from 0.6 to 1.3, ϕ_0 increases from 0.004 to 0.7.

For many systems, βe_{ii} are in the range $(-0.50,\ -0.70)$, as discussed at length elsewhere [25]. Therefore, we can safely take the values of w_{M0} and w_{E0} around 0.75 [see Eq. (3.4)]. The exchange energy between the middle and end groups, however, will be small due to cancellation [see Eq. (2.6)] and therefore w_{ME} will be close to 1. From now on, whenever we speak of interactions, we refer to the exchange interactions ε_{ij} and not to the direct interactions e_{ij}, unless noted otherwise.

We begin by noting that for any coordination number of the lattice that we choose, the end groups always have one extra unbonded contact as compared to the middle group. When the end and middle groups are chemically similar, it is clear that the origin of the difference in the free volume of the end and middle group is due to finite coordination number, and it is obvious that the end groups will always have more free volume. We can make the two groups chemically similar or identical by setting $w_{ME}=1$ and $w_{M0}=w_{E0}=w$. Also, a special case is the athermal limit where all three $w_{ij}=1$. In Fig. 1, we set $z_0=0.2$, $q=8$, $M=100$, and $w_{ME}=1$. We note that with $v_0 \cong (10\,\text{Å})^3$ and at room temperature, the choice of $z_0 \cong 0.2$ corresponds to $\cong 1$ atm pressure. We display the results for v_{ex} over a range of values for w. We find that the end group has more free volume than the middle group, a foreseen result.

We consider the effect of the coordination number, the pressure, the molecular weight, and the three interaction strengths on v_{ex}. We first demonstrate the effects of considering different coordination numbers. In Fig. 2 we show the behavior of v_{ex} as a function of the coordination number from $q=4$ to 12. It is obvious that as the coordination number increases, the extra unbonded contact available to the end group will be progressively inconsequential. Thus we would expect the difference in the free volume of an end group and middle group to diminish, even in the case where the two are chemically similar, as the coordination number is increased.

If one takes the following viewpoint, which does not seem far fetched, that more flexible the polymers are, higher the ‘‘coordination number’’ for the corresponding lattice model, then we conclude that the difference v_{ex} decreases as the flexibility increases. This, then, suggests that the effect of decreasing the molecular weight on the glass transition for flexible chains would not be as strong as that for rigid chains.

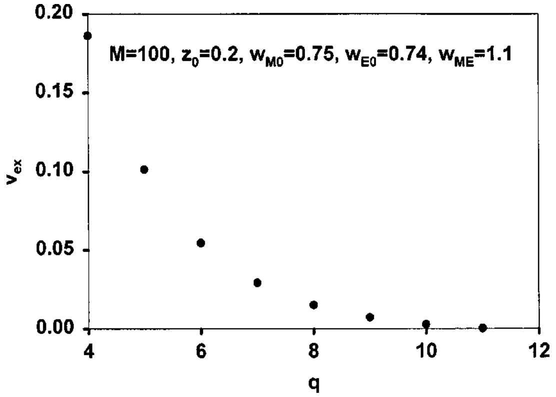

FIG. 2. Effect of coordination number on v_{ex}. As q is increased from 4 to 11, ϕ_0 decreases from 0.16 to 0.01.

Next, we consider the effect of pressure and w_{M0}. In Fig. 3 we plot v_{ex} as a function of z_0, the reduced pressure, for different combinations of interactions. It is evident that at fixed temperature, with increasing pressure v_{ex} may increase (●) or decrease (○, ▼, ▽). Thus, the effect of decreasing pressure (which controls the void density) is merely to enhance the magnitude of v_{ex} while its sign is governed largely by the interactions.

The role of w_{M0} is twofold. Figure 4(a) and 4(b) pertain to the effect of middle-group/void interaction. In Fig. 4(a) we plot v_{ex} against w_{M0} for different choices of $w_{ME}=0.9$(●),1(○),1.1(▼)). Figure 4(b) displays the changes in the void density—ϕ_0(◇), v_M(●), and v_E(▽)—with w_{M0} for a specific case, $w_{ME}=1.1$ of Fig. 4(a). Figure 4(b) also contains other plots; however, those will be discussed later. For ϕ_0, v_M, and v_E, the axis on the left-hand side is to be considered. Because the middle groups constitute a large fraction of the polymer, the value of w_{M0} also controls the void density. As $w_{M0} \rightarrow 0$, the statistical weight of states with larger N_{M0} rapidly diminishes, i.e., the void density goes to zero [see Fig. 4(b)]. As the void density decreases, v_{ex} is also expected to decrease because v_E and v_M themselves decrease and get closer to zero. From Fig. 4(a) we find

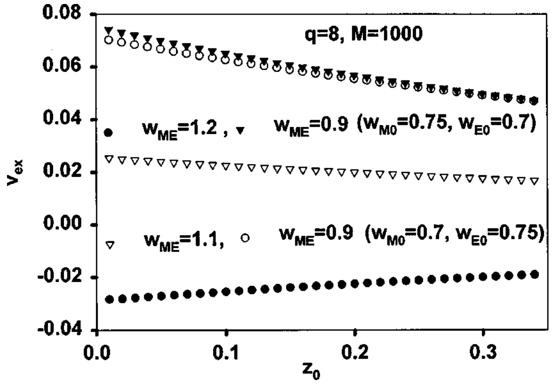

FIG. 3. Effect of pressure on v_{ex} for four different systems. As z_0 is increased from 0.01 to 0.34, ϕ_0 decreases from $\sim$0.047 to $\sim$0.015 in all cases.

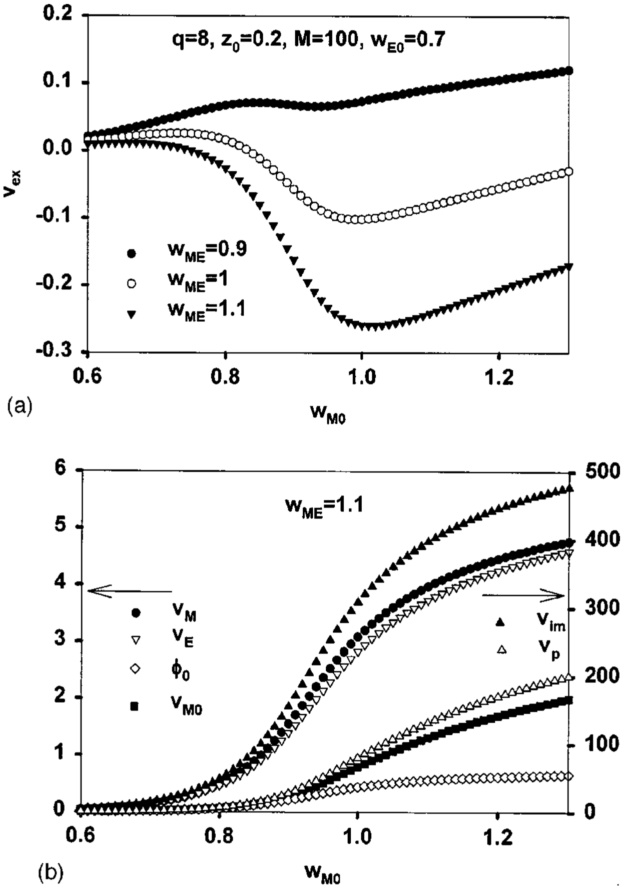

FIG. 4. (a) Effect of midvoid interaction on v_{ex} for different choices of w_{ME}. (b) v_M, v_E, and the different characteristic free volumes for a specific case $w_{ME}=1.1$. As w_{M0} is increased from 0.6 to 1.3, ϕ_0 increases from ~ 0.005 to ~ 0.7 in all cases.

that at $w_{M0} \cong 0.6$, $v_{\mathrm{ex}} \cong 0$ irrespective of the choice of w_{ME}. Thus, v_{ex} will reach the value of zero asymptotically as $w_{M0} \to 0$. Second, we have three interactions and, therefore, the behavior of v_{ex} is expected to depend on the relative magnitude of w_{M0}, w_{E0}, and w_{ME}. The changes in their relative magnitudes gives rise to the features of maximum and minimum in v_{ex} [refer to Fig. 4(a)] due to the difference in the rate of change of free volume of the end group and middle group with w_{M0}. If the free volume of an end group rises faster than that of a middle group, v_{ex} rises and a maximum is seen. However, if the free volume of a middle group rises faster than that of an end group, v_{ex} decreases and a minimum is observed. For example, in Fig. 4(b) the difference between v_M(●) and v_E(▽) first increases with w_{M0} and then decreases (the changes in the difference are not easily discernible), which results in the minimum in v_{ex}(▼) in Fig. 4(a). However, the maximum and minimum may become more or less pronounced or even disappear by changing the parameters. Consider a specific case, e.g., Fig. 4(a) (●) with $w_{ME}=0.9$. As w_{M0} is incremented from 0.6 to 0.7, in every instance $w_{M0}<w_{E0}$ (except at $w_{M0}=0.7$) and hence the contacts between the end groups and voids are favored over the contacts between the middle groups and voids. Also, the void density increases rapidly as w_{M0} is incremented.

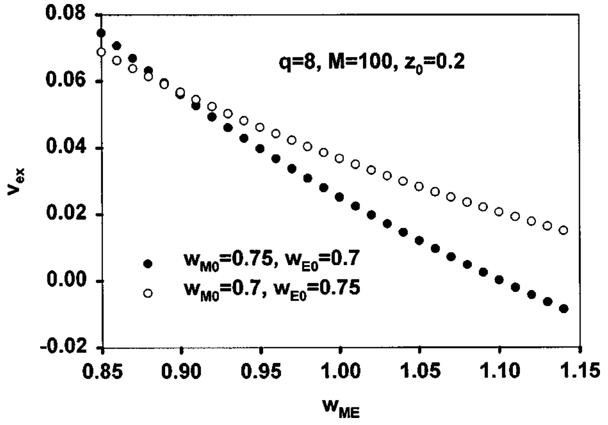

FIG. 5. Effect of w_{ME} on v_{ex} for the choices of $w_{M0}>w_{E0}$ and $w_{M0}<w_{E0}$. As w_{ME} is increased from 0.85 to 1.14, ϕ_0 decreases from ~ 0.03 to ~ 0.02 in both cases.

Due to these two reasons, we find that v_{ex} increases with increasing w_{M0}. However, when $w_{M0}>w_{E0}$, the effect is reversed and therefore the maximum is obtained at $w_{M0} \cong 0.85$ after which v_{ex} begins to decrease. Of course, the maximum is not expected to be exactly at $w_{M0}=w_{E0}$ because v_{ex} is a function of other parameters too.

We have explained that for some large value of w_{M0} (mainly determined by the choice of w_{E0} and w_{ME}) v_{ex} must begin to decrease with increasing w_{M0}. Our calculations show that as w_{M0} is incremented further, finally a minimum is obtained beyond which v_{ex} begins to rise and eventually approaches the value of 1.0 asymptotically in the limit $w_{M0} \to \infty$. The maximum and minimum is readily visible in Fig. 4(a) (●). In the other two plots, the maxima have been suppressed due to the choice of interactions. The eventual rise in v_{ex} can be understood by noting that the end group has one extra unbonded contact available. When w_{M0} becomes very large as compared to w_{E0} and w_{ME}, the voids are strongly attracted to the middle groups. Because the end groups are attached to the middle groups, they too get their share of voids and at this stage the actual value of w_{E0} and w_{ME} becomes immaterial. Hence, both v_M and v_E increase with increasing w_{M0}, e.g., if we choose $q=8$, then as $w_{M0} \to \infty$, $v_E \to 7$ and $v_M \to 6$; therefore $v_{\mathrm{ex}} \to 1.0$. We also note that ϕ_0 decreases as the attractive direct interaction strength e_{MM} increases, i.e., as w_{M0} decreases. According to the Doolittle semiempirical equation, this corresponds to an increasing viscosity. As a consequence, T_g must increase with the strength of e_{MM}.

By comparing the three results obtained for different choices of w_{ME} in Fig. 4(a), we find that the nature of the middle-group/end-group interaction perhaps has the strongest effect on v_{ex}. In Fig. 5, we show v_{ex} as a function of w_{ME} for two cases, $w_{M0}>w_{E0}$(●) and $w_{M0}<w_{E0}$(○). We find that irrespective of the interactions w_{M0} and w_{E0}, as w_{ME} is increased, v_{ex} decreases, i.e., the middle groups tend to have more free volume. This behavior can be explained with the argument that as the middle-group/end-group interaction becomes attractive ($w_{ME}>1$), the end groups are surrounded by the middle groups of its own chain or other

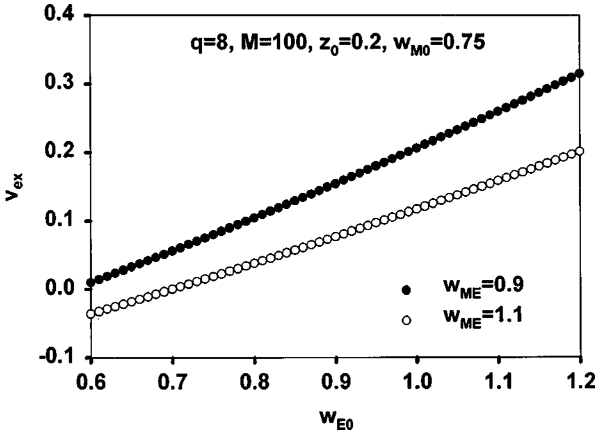

FIG. 6. Effect of end-void interaction on v_{ex} for two choices of w_{ME}. As w_{E0} is increased from 0.6 to 1.2, ϕ_0 increases from ~0.03 to ~0.04 in both cases.

chains and are therefore effectively ''shielded'' from the voids. Due to the fact that the middle groups greatly outnumber the end groups, the effect of this shielding is more severe on v_E than v_M (since these denote the average values). Therefore, as the middle-group/end-group interaction becomes more attractive, v_E decreases faster than v_M and therefore v_{ex} decreases. When the middle-group/end-group interaction becomes repulsive, contacts with the voids are favored and then v_{ex} increases. The relative values of w_{M0} and w_{E0} determine the rate of change of v_{ex} with w_{ME}. When $w_{E0}<w_{M0}$, the middle groups prefer to be with the voids and hence v_{ex} decreases more rapidly with w_{ME}. We have considered the effect of pressure and molecular weight also but we find that the qualitative relation between v_{ex} and w_{ME} remains unchanged.

Figure 6 displays the effect of end-group/void interaction on v_{ex}. It is clear from the figure that for a fixed choice of w_{ME} and w_{M0}, as the end-group/void interaction is made attractive, v_{ex} increases, i.e., the end groups tend to have more free volume. It is also evident that having the middle-group/end-group interaction attractive decreases v_{ex} and reduces the rate of increase of v_{ex} with w_{E0}. Although we have not shown it here, we have also investigated the effect of all other parameters (besides middle-group/end-group interaction) on the qualitative relation between w_{E0} and v_{ex}. We find that v_{ex} increases with w_{E0} irrespective of the choice of the interactions, pressure, molecular weight, etc.

The effect of molecular weight is considered in Fig. 7 by considering four different combinations of middle-group/void, end-group/void, and middle-group/end-group interactions. Different combinations have been chosen to cover all the features, based on our understanding of the interplay of these interactions. From Fig. 7 we immediately note that v_{ex} has a weak molecular weight dependence, especially in the high molecular weight limit. It is also apparent that at fixed pressure and temperature, v_{ex} may increase (▼) or decrease (●, ○, ▽) as molecular weight is incremented. Thus, the effect of molecular weight is dependent on the choice of parameters, similar to the effect of pressure.

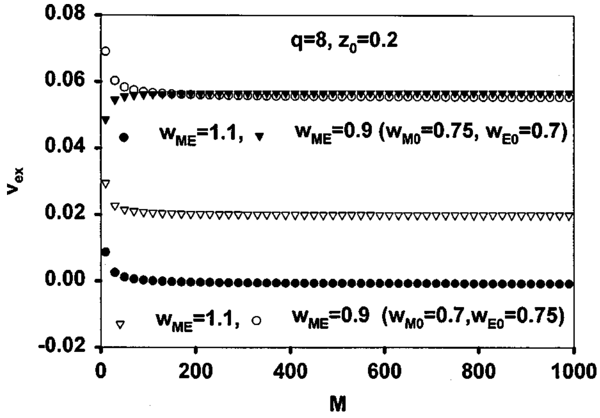

FIG. 7. Effect of molecular weight on v_{ex} for four different systems. As M is increased from 2 to 982, ϕ_0 decreases from ~0.08 to ~0.02 for $w_{M0}<w_{E0}$, and from ~0.04 to ~0.036 for $w_{M0}>w_{E0}$.

V. DISCUSSION AND CONCLUSIONS

Experimental methods that are widely used to estimate and characterize free volume are positron annihilation spectroscopy (PAS), fluorescence spectroscopy, and photochromic labeling technique. Small angle x-ray and neutron diffractions have also been used to determine density fluctuations and then to deduce free volume size distributions. Of these methods, fluorescence spectroscopy and photochromic labeling technique have the capacity to estimate local free volume. Sung, Yu, and Robertson [24] have employed photoisomerisable probes to evaluate the free volume at different sites along the polymer molecule. The probes—azobenzene chromophores—undergo a trans→cis photoisomerization, the extent and kinetics of which are sensitive to the local free volume immediately surrounding the probe. From the photoisomerization behavior at different sites, the local free volume at each site can be estimated. Therefore, the local free volume they investigate is similar to our definition of free volume associated with a group. They investigated the regions around the chain ends, the chain sides, and the chain centers along the backbone of polystyrene. Through an indirect analysis, they were able to conclude that the styryl end groups have more free volume than the middle groups. It should be noted that for this system, the end groups are very similar to the middle groups and therefore the above result is expected, as seen in our theory.

Danusso *et al.* [26,27] were particularly interested in studying the effect of end-group dissimilarity on the variation of T_g with molecular weight. They measured the T_g for 17 series of linear perfluoro-poly(oxymethylene-co-oxyethylene) oligomers of several molecular weights having a common perfluoronated body and equal end groups of different types. A clear end-group effect is demonstrated in their results in which the T_g increased with decreasing molecular weight for several oligomers. The unexpected results were obtained mainly for systems in which the end groups were polar in nature (opposite in nature to the hydrocarbon backbone molecules), causing a stronger direct end-end attractive interaction. The stronger attraction corresponds to a smaller w_{E0}. Interpretation of these new results in terms of the free volume model implies that the fractional free volume for these systems must decrease with decreasing molecular weight, an effect that is possible when the end groups have less free volume (small w_{E0}) than the middle groups. However, Danusso *et al.* ascribe their unusual results to changes in the cohesive state of the system with molecular weight due to the different interaction strengths between the middle groups, the end groups, and each other. Similar arguments have been propounded by Engberg *et al.* [28], who have studied the effect of end groups on the structural relaxation behavior of poly(propylene glycol) (PPG), using Brillouin scattering and dielectric relaxation. They find that the relaxation dynamics of hydroxyl (OH)-terminated systems are rather insensitive to molecular weight whereas with methyl (CH_3)-terminated systems a large change in the relaxation dynamics with molecular weight is observed. The difference in behavior has been related to hydrogen bonding, due to which the effective chain length purportedly increases, and then one probes the segmental relaxation time, which is almost independent of the degree of polymerization. Other groups [29–31] have investigated the effect of having an ionic end group on the viscosity and glass transition temperature. In these systems too, unusual results of increasing viscosity and T_g with increasing end-group concentration have been reported. In general, these results have been attributed to the aggregation of the ionic groups thereby forming cross-linked networks which, in effect, leads to a reduction in segmental mobility. Thus, substantial evidence [24,26–34] of the strong effect of the nature of end groups on physical properties is present in the literature. From the above discussion it is apparent that the free-volume model, although useful, cannot account for molecular dynamics in entirety. The free volume is only a secondary effect; at the most fundamental level it is the interactions that control the dynamics. Furthermore, the ambiguity in the definition of free volume or the often used term ''dynamic free volume'' (the part of free volume that is relevant for dynamics) has lead to considerable confusion and difficulty in implementing the theory. We have defined the free volume associated with a group as the average number of voids in its immediate proximity. Clearly, this free volume is the most relevant while considering instantaneous molecular mobility. However, long-range cooperative relaxation will be governed by both, the free volume associated with individual groups as well as the total free volume in the system. This is because cooperative relaxation is also facilitated by the presence of a cluster of voids, an information that is not present in our definition of free volume associated with a group. In an attempt to characterize the overall free volume in the system, we have introduced the following definitions as different measures of the characteristic free volume in the system.

$$v_{\rm im}=(M-2)v_M+2v_E, \quad v_{M0}=\phi_0/\phi_m, \quad v_p=\phi_0/\phi_n,$$

and, of course, the fractional free volume ϕ_0. Here, $v_{\rm im}$ is the free volume that is *immediately* neighboring or surrounding the polymer molecule, v_{M0} denotes the average free volume available to every monomer, and v_p is the average free volume per polymer molecule. The number density of polymer molecules is $\phi_n=\phi_m/M$. We have studied these different definitions in Fig. 4(b). For $v_{\rm im}$(▲) and v_p(△), the axis on the right-hand side applies, while for v_{M0}(■) and ϕ_0(◇), the left-hand side axis is to be considered. For this particular example we find that $v_{\rm im}$, v_{M0}, v_p, and ϕ_0 all increase with increasing w_{M0}. Thus different measures of the characteristic free volume give similar results. However, this is not true in general. We find (results not shown) that the above four definitions can give conflicting results for the changes in the characteristic free volume when considered as a function of the interactions, molecular weight, pressure, etc. Also, from Fig. 4(b) we find that the functional form and magnitudes of $v_{\rm im}$, v_{M0}, v_p, and ϕ_0 are quite different. Thus the definition of characteristic free volume, which is relevant for mobility, must be chosen carefully. Voids that are shared (i.e., are common) between two or more monomers contribute towards instantaneous motion of an individual group or segment, but may not significantly contribute towards long-range relaxation, because the segments have to return to their original position. However, with neighboring cluster of voids that are large enough, the chains can move more easily and quickly. To complete the free-volume approach, in addition to the total free volume, the idea of the size distribution of free volume has been invoked. Theoretical [8–10] and experimental [22,34–37] results for the size distribution of void clusters have been obtained for several systems. However, we believe that consideration of free volume alone is insufficient to describe molecular dynamics and one must account for the interactions. We have carried out calculations for the size distribution of void clusters in our scheme. The results will be presented elsewhere [38].

In summary, we have demonstrated that for systems in which the end group is chemically dissimilar from the middle group, the middle group may have more free volume than the end group, in contrast to popular belief. When the two groups are similar, the end group will generally have more free volume than the middle group. The factors that are in favor of the middle group having more free volume over an end group are: attractive end-end and middle-middle-direct interaction and attractive middle-end exchange interaction and vice versa. In the experimental results that we have quoted, the systems that showed unusual behavior in general have an attractive end-end direct interaction. The effect of pressure and molecular weight can be of either type and appears to be dependent on the interactions.

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