PHYSICAL REVIEW E VOLUME 54, NUMBER 2 AUGUST 1996

Entropy of glassy polymer melts: Comparison between Gibbs-DiMarzio theory and simulation

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(Received 28 November 1995)

We calculate the free energy of a model for a polymer melt in a computer simulation of the bond-fluctuation model and determine the entropy of the melt over a wide range of temperatures, including the region close to the glass transition. The results are compared with the Gibbs-DiMarzio theory, a theory by Flory for semiflexible polymers, and a modification of their theories due to Milchev. We can describe the data within the framework of the Flory theory with Milchev's correction and discuss the consequences for the understanding of the glass transition. [S1063-651X(96)04407-8]

PACS number(s): 61.20.Ja, 64.70.Pf, 61.20.Lc

I. INTRODUCTION

A challenging problem in condensed matter physics is to develop a detailed understanding for the structural glass transition [1–3]. The existing theoretical approaches can roughly be divided into two classes: Some theories regard the calorimetric glass transition as a consequence of a dynamic anomaly which already occurs in the supercooled state of the liquid at temperatures above the glass transition temperature T_g (e.g., mode-coupling theory [4–6]), while other theories try to relate it to a thermodynamic phase transition, the clear signature of which is blurred by the finite experimental observation time. Examples for these latter theories are the free-volume theory [7] for liquids of all kind, including polymeric systems, and the Gibbs-DiMarzio theory which is especially designed for polymer melts [8–14].

If we write the canonical partition function as

$$Z=\sum_{E} \Omega_{\mathrm{GDM}}(E,N,V)e^{-\beta E},$$

the Gibbs-DiMarzio theory is concerned with calculating the microcanonical partition function $\Omega_{\mathrm{GDM}}(E,N,V)$. In this calculation it turns out that one finds $\Omega_{\mathrm{GDM}}(E,N,V)<1$ for certain combinations of N, V, and E. In the thermodynamic limit we can replace $\Omega_{\mathrm{GDM}}(E,N,V)$ by $\Omega_{\mathrm{GDM}}(\langle E/N\rangle,\langle V/N\rangle)$ and view $\langle E/N\rangle$ and $\langle V/N\rangle$ as functions of temperature. If now upon cooling one reaches values of $\langle E/N\rangle$ and $\langle V/N\rangle$ for which $\Omega_{\mathrm{GDM}}<1$, an entropy catastrophe occurs, which is the theoretical counterpart of the experimental ''Kauzmann paradoxon'' [15,16]. It is an appealing feature of this theory that it thus connects the occurence of a glass transition at T_g with a vanishing entropy of the supercooled melt at a finite temperature $T_2<T_g$.

Based on the formula for Ω_{GDM} several predictions for the glassy behavior of polymeric systems can be derived. Some of these predictions have been subject to experimental scrutiny, e.g., T_g as a function of pressure [17] or of molecular weight [9,18–21] and the discontinuity of specific heat at T_g [22,23]. In addition to that, the predictions about the influence of cross-links [24–26] and plasticizer [27] have been investigated, and the theory has also been applied to copolymers and polymer mixtures, where T_g depends on the composition [28]. In all these cases the experimental data can be described in the framework of the Gibbs-DiMarzio theory rather well.

With the present work we want to present a further test of the theory, in which not a derived, but the basic theoretical quantity, i.e., the density of states or equivalently the configurational entropy of the melt, is in the center of interest. If the entropy of a polymer melt is known over the range of temperatures from the liquid to the supercooled state, the approximation of the Gibbs-DiMarzio theory and of other related theories can be tested and critically compared. Therefore we determined the entropy of a glassy polymer melt by Monte Carlo simulation. Since the method was discussed in detail in Ref. [29], we focus in this paper on a comparison between theory and simulation.

The paper is organized as follows: In Sec. II we repeat some aspects of the model and discuss the necessary input parameters. Section III presents several theoretical approximations for the entropy and compares them with the simulation data. Section IV discusses the results and the consequences for the understanding of the glass transition.

II. MODEL AND SIMULATION

The model of our simulation is the bond-fluctuation model (BFM) in three dimensions [30,31]. This is a lattice model for polymers which mimics the properties of a continuum model, e.g., a widespread distribution of bond angles between the monomers. Each monomer occupies eight sites of a simple cubic lattice, forming a cube (see Fig. 1). We choose a lattice of 30^3 sites and put $K=180$ chains of length $N=10$ on it. The density of occupied lattice sites is

$$\rho=\frac{8KN}{L^3}=0.5\overline{3}. \tag{1}$$

Previous work demonstrated that the system with this density behaves like a polymer melt [31–33]. Between monomers there is excluded volume interaction. Monomers in a chain are connected by bond vectors. These bond vectors

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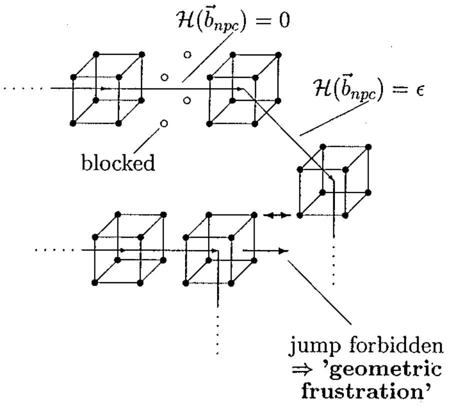

FIG. 1. A possible configuration of monomers in the melt. The blocked sites cannot be occupied by monomers due to the self-avoidance of the monomers. The corresponding bond is in the ground state. The sketched jump would also violate the condition that no site can be occupied by more than one monomer. So it is impossible for the bond to reach the energetically favorable state.

are not arbitrary, but generated from a set of six basic vectors by permutations and reflections of the coordinates, denoted by [ ]. The basic vectors are

$$[2,0,0],[2,1,0],[2,1,1],[2,2,1],[3,0,0],[3,1,0]. \tag{2}$$

This special choice ascertains that chains cannot cross each other during the course of their motion with simple random-hopping dynamics [30]. There is an important consequence of this set of vectors. Figure 1 shows a portion of a typical configuration of the melt. Let us look only at the two upper monomers and the bond in between. The bond is in the state [3,0,0], creating a layer of empty lattice sites between the monomers. These lattice sites cannot be occupied by another monomer, since this requires a set of eight unoccupied sites forming a cube. Thus they are lost as available volume. A bond in the state [3,0,0] blocks four sites of the lattice, a bond in the state [3,1,0] blocks two sites. A complete occupation of the lattice is only possible if bonds of these two types are avoided. Due to their presence the actually effective density of a configuration differs from Eq. (1). Such an effective density can be defined in the following way: In the equilibrated melt, consisting of K chains of length N, additional monomers are inserted one after the other, until the lattice is filled. During the insertion the chains are not allowed to rearrange. The maximum number H (''holes'') of insertable monomers is determined and used to define an effective density ρ_{eff} via

$$\rho_{\mathrm{eff}}=\frac{KN}{M}, \tag{3}$$

where $M=KN+H$ denotes the total number of monomers and holes in the system. This quantity is averaged over several independent configurations at each temperature. In this way we model the solvent molecules as particles of the same exclusion volume as the monomers of our chains. The effective density does not depend only on the number of chains, but also through H sensitively on temperature, as we will see later. Since H is directly connected to the accessible free volume, the temperature dependence of ρ_{eff} reflects the change of the monomer mobility with progressive supercooling and is therefore a more important quantity for the present model than ρ of Eq. (1).

Temperature is introduced into the system via a simple two-level Hamiltonian. Each bond can have only two values of energy: 0, if the bond is in state [3,0,0] and ϵ otherwise, i.e.,

$$\mathcal{H}=\begin{cases}0 & \text{if } \mathbf{b}\in[3,0,0]\\ \epsilon & \text{otherwise.}\end{cases} \tag{4}$$

In the following a bond in the state [3,0,0] will be called a ''bond in the ground state,'' a bond in another state will be called ''excited.'' The degeneracy of the ground state is $g_0=6$ and that of the excited state is $g_\epsilon=102$. This Hamiltonian has the following consequence: Since a bond of type [3,0,0] blocks additional lattice sites, the free volume and the mobility of the chains is reduced. The more bonds are in this state, the smaller the diffusion constant of the melt. This mechanism is responsible for the glasslike freezing of the melt for $T<0.2$ if relaxation is performed with simple ''hopping dynamics'' [34]. For $T\geqslant0.25$ the diffusion coefficient of a chain can be determined reliably and fitted by a Vogel-Fulcher equation, yielding a rough estimate of $T_0\approx0.17\pm0.02$ for the absolute freezing point of the model [32–34]. In order to judge the significance of this value, it has to be emphasized that the diffusion coefficient decreases only by two orders of magnitude with respect to its high temperature value in the accessible range $T\geqslant0.25$. Therefore the value, $T_0\approx0.17$, is the result of a *high temperature extrapolation,* which is likely to overestimate the absolute freezing point of the model considerably. Similar observations were also made in a recent experimental study [35]. The value $T_0\approx0.17$ should thus not be interpreted as an accurate result for the Vogel-Fulcher temperature, but rather as an estimate for the interesting temperature region, where one can expect the model to exhibit glassy behavior. Despite these drawbacks in the precise location of T_0 the structural relaxation of the studied polymer melt slows down drastically for $T\leqslant0.25$, which makes a proper equilibration of the melt on all length scales of a polymer by single-monomer dynamics unfeasible in practice. Therefore we use the slithering-snake algorithm, which allows us to measure *static* properties down to $T\approx0.16$ [36].

Figure 2 shows the effective density ρ_{eff} as a function of inverse temperature. The effective density ρ_{eff} is always larger than the volume fraction of occupied lattice sites ρ, even at $T=\infty$. This is caused by the equilibrium population of bonds in the states [3,0,0] and [3,1,0], which prevents the monomers from packing as closely as possible, and the amorphous structure of the melt. When the melt is cooled down, the Hamiltonian favors the class [3,0,0] and the effective density has to increase further. To illustrate this point from another perspective Fig. 3 shows the ratio f of excited bonds as a function of inverse temperature. In the athermal case $f(T=\infty)=0.964$, which is very close to $f=g_\epsilon/(g_0+g_\epsilon)=102/108\approx0.944$, the estimate of an isolated two-level system. Evidently, at $T=\infty$ the influence of the density on f is rather small. This influence becomes larger with cooling. In the limit $T\rightarrow0$ no bond should be

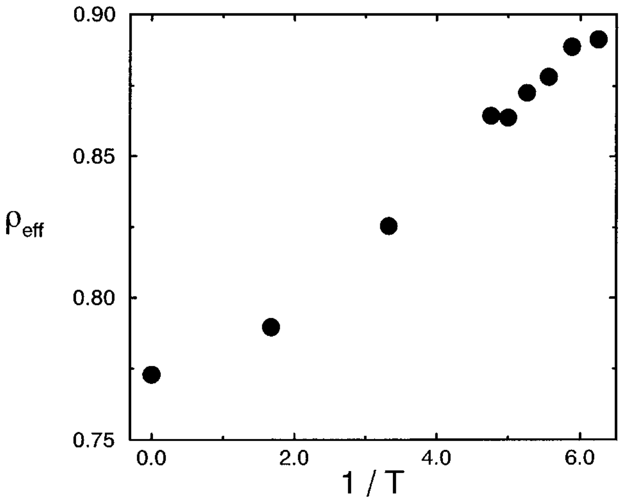

FIG. 2. The effective density ρ_{eff} vs inverse temperature $\beta=1/T$. In this and all further figures T is already a reduced temperature measured in units of k_B/ϵ [see Eq. (4)]. The effective density ρ_{eff} is dimensionless due to the definition in the text.

excited and f should vanish. We see that there is a saturation effect at very low temperatures. f always has a value slightly larger than 0. The reasons for this are packing constraints of the melt. Not all bonds can reach the ground state simultaneously. A typical example for such a configuration can be seen in Fig. 1. The bond at the bottom cannot enter the state [3,0,0] without violation of the excluded volume interaction. This *frustration* is responsible for the glass transition in this system [33]. As in the original model of Gibbs and DiMarzio, we deal here with a lattice model, where a temperature decrease leads to an increase of (effective) density and a local stiffening of the chains. But unlike the original model, a strong tendency to liquid crystalline short range order is avoided. Such short range order was found in other Monte Carlo (MC) studies [37] and is an undesirable side issue.

Another important input parameter for the subsequent analysis is the coordination number z, i.e., the number of nearest neighbors of a monomer, which is related to the pair-correlation function. This function was investigated for $T=\infty$ and $\rho=0.42$ in Ref. [30], and for the present thermal model in Ref. [33]. Both studies found two distinct minima at distances $r=\sqrt{6}$ and $r=\sqrt{10}$ (measured in units of the lattice constant). These minima allow the definition of z for the BFM as the number of nearest neighbors with $r\leqslant\sqrt{6}$ or $r\leqslant\sqrt{10}$. We prefer the latter choice, since it warrants that predecessor and successor of a monomer in the same chain are always counted as nearest neighbors. In view of a later comparison with the Gibbs-DiMarzio theory a nearest neighbor is taken to be either a monomer or a hole on the lattice. This definition yields a value larger than that resulting from an integration over the first peak of the pair-correlation function and also larger than that used by Müller *et al.* in their studies of binary polymer mixtures [38,39], where an interaction range of $\sqrt{6}$ was used and only monomers belonging to different chains were considered, as is appropriate in this different context. The coordination number z as a function of inverse temperature can be seen in Fig. 4. For very low temperatures z is only slightly larger than 11. For high temperatures z adopts a value of about 12. Such a value is typical of a dense packing of hard spheres and reflects the fact that our model mimics the properties of polymers in continuous space rather closely. With decreasing temperature the coordination number decreases only by about 1, although the population of the ground state increases strongly. This shows that the stretching of the bond vectors perturbs the average distribution of monomers and holes around a monomer only slightly.

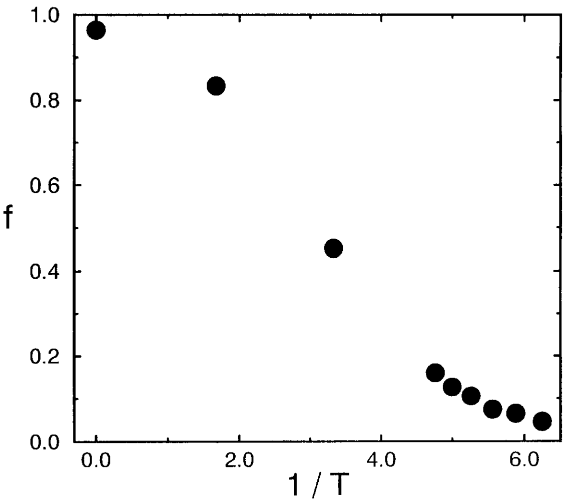

FIG. 3. The ratio f of bonds in an excited state vs the inverse temperature $\beta=1/T$.

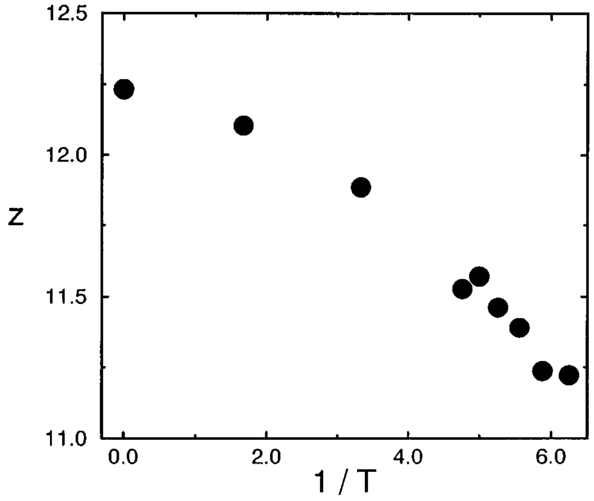

FIG. 4. The coordination number z vs the inverse temperature $\beta=1/T$.

Finally, the free energy and from that the canonical entropy has to be determined for the model under consideration. The first step towards the free energy is the measurement of the excess-chemical potential. This is done by a modification of Widom's particle insertion method [40–42] and its extension to thermal systems [29]. The excess-chemical potential in combination with the partition function of a single chain leads to the free energy of the system [29,41]. The partition function of the single chain is measured in a MC-simulation by an algorithm proposed by Kumar, Szleifer, and Panagiotopoulos [43], which can easily be applied to the BFM [29]. With the help of the free energy the additional measurement of the internal energy finally yields the temperature and density dependence of the entropy. Since the method and the raw data have already been presented in Ref. [29], we restrict ourselves in the following to the physical interpretation of the results and focus on the comparison with various theoretical predictions for the entropy.

III. APPROXIMATIONS FOR THE ENTROPY

The theoretical approximations we want to discuss differ in the choice of the thermodynamic ensemble they are done in. The first one, the pressure-trimer approximation, is done in the canonical ensemble, same as the simulation.

The various more elaborate theoretical approaches by Flory, Milchev, and Gibbs-DiMarzio are calculations in the microcanonical ensemble. The entropy density as calculated in this ensemble can differ from the simulation value by an amount of the order $O(R^{-1/2})$ if there are R degrees of freedom in the system. Since $R \approx 2 \times 10^3$ we can expect deviations of $2 \ldots 3\%$ which is much less than any effect that we will discuss.

A. Pressure-trimer approximation

The equilibrium properties of the studied polymer model result from the competition between the intrachain energy and the density of the melt. Approximately, the effects of the density can be taken into account by balancing the volume requirements of subunits, consisting of three successive monomers along the chain, with the pressure that is exerted by the melt at the given density [44]. Since such a ''pressure-trimer approximation'' (PT-approximation) yields rather accurate estimates for the chain length and temperature dependence of various quantities that probe different length scales of the polymer (bond length, radius of gyration, etc.), it seems worthwhile to apply this simple approach also to determine the entropy.

The starting point of the PT-approximation is the calculation of the exclusion volume $v(i,j)$ for all trimers (i,j) which can be constructed from the set of allowed bond vectors [see Eq. (2)]. The exclusion volume is defined as the volume which is blocked for other monomers by the excluded volume interaction (i.e., four sites for a bond in the ground state; see Fig. 1). If a trimer changes its configuration, the exclusion volume will fluctuate. Such a fluctuation can only occur if the arrangement of the adjacent monomers provides the required space. Hence the local monomer density limits the number of available configurations and thereby the *density of states* of a trimer in the canonical ensemble. The simplest way of representing the effect of the surrounding monomers is to regard the changes in the exclusion volume as if they were *macroscopic volume fluctuations*. The probability of a macroscopic fluctuation of size ΔV in a system at pressure p is proportional to $\exp[-\beta p \Delta V]$. Accordingly, we choose the density of trimer states as $\exp[-\pi^* v(i,j)]$, where π^* is the (osmotic) pressure of the *athermal* BFM, whose chain length and density dependence is known analytically [45]. Therefore the (canonical) partition function of a trimer in this approximation reads [44]

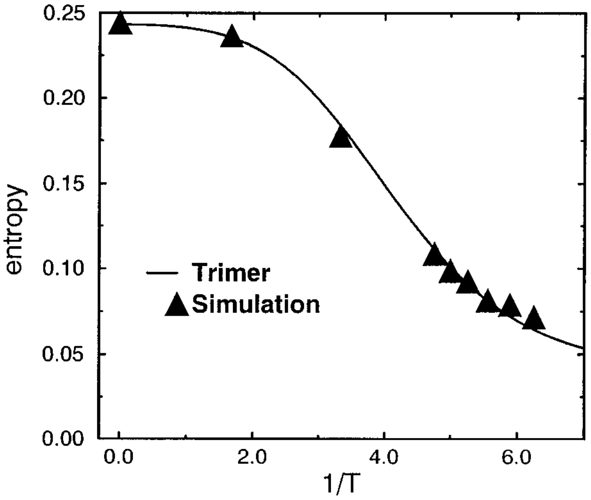

FIG. 5. Comparison of the temperature dependence of entropy per lattice site s with the PT-approximation [solid line; see Eq. (6)]. s is measured in units of k_B.

$$Z_{\mathrm{PT}}(\beta,\rho) = \sum_{ij} \exp\{-\pi^*(\rho) v(i,j) - \beta[\mathcal{H}(\mathbf{b}_i) + \mathcal{H}(\mathbf{b}_j)]\}, \tag{5}$$

where the sum runs over all bond pairs compatible with the excluded volume constraints. With the help of Eq. (5) the PT-approximation for the entropy can be written down immediately as

$$\begin{aligned} S_{\mathrm{PT}}(\beta) &= \beta[E_{\mathrm{PT}}(\beta) - F_{\mathrm{PT}}(\beta)] \\ &= \beta\langle \mathcal{H}(\mathbf{b}_i) + \mathcal{H}(\mathbf{b}_j)\rangle + \ln Z_{\mathrm{PT}}(\beta). \end{aligned} \tag{6}$$

Since a chain with $(N-1)$ bonds yields $(N-1)/2$ trimers, the entropy per lattice site is given by $s_{\mathrm{PT}} = K(N-1)S_{\mathrm{PT}}/2L^3$. The result of this calculation is compared with the simulation data in Fig. 5. One can see that the PT-approximation describes the temperature dependence of the entropy almost perfectly from $T=\infty$ down to $T \sim 0.18$ ($\beta \approx 5.5$). This shows that the impact of the complicated many-body effects which determine the configurational statistics of the melt are grasped, to a good approximation, by the influence of the pressure on the bonds in the whole temperature range except for very low temperatures (i.e., for $T < 0.18$). Since the temperatures below $T = 0.18$ belong to the region close to the glass transition of the studied model [34], the deviation between the PT-approximation and the simulation data suggests to test whether the Gibbs-DiMarzio theory or related theories can provide a better description. These different approximations for the entropy are exposed and compared with the simulated entropy in the subsequent sections.

B. Flory's approach

Our exposition of the following three theoretical approximations for the partition function of a dense polymer melt will follow closely a discussion by Wittmann [46], who analyzed in detail these theoretical approaches and their interrelation.

The purpose of Flory‘s original work [47–49] is the description of semiflexible lattice polymers in solution. In this model every monomer occupies one lattice site. Flory focused on the temperature driven transition from flexible to collinear chains. A collinear bond angle is said to have energy 0, a flexed one energy ε. The behavior of the melt is characterized by a single temperature dependent parameter, the flexibility f_F, which is defined as the probability that two successive bonds in a chain are not collinear

$$f_F=\frac{(z-2)e^{-\beta\varepsilon}}{1+(z-2)e^{-\beta\varepsilon}}. \tag{7}$$

By construction this parameter describes the transition from flexible chains at high temperature $[f_F\approx(z-2)/(z-1)]$ to collinear chains for $T\rightarrow 0$ $(f_F\rightarrow 0)$. This definition separates the possible types of trimers into two classes and introduces a two-level system: trimers with collinear (ground state) and with flexed bonds (excited state).

A chain with N monomers has $(N-1)$ bonds and $(N-2)$ bond angles which can have an energy. This definition is only reasonable on the simple cubic lattice. On the generalized tetrahedral lattice all trimers are equivalent and thus one arbitrarily chosen trimer has to be distinguished. But a simple symmetry operation turns this trimer into another, which should have the same energy. So no energy can be associated with the first bond angle in this case and only $(N-3)$ bond angles can contribute to the energy. That leads to different factors in the two formulations of the theory, but otherwise does not affect the results. Since we work on a simple cubic lattice, we use Flory's result with $(N-2)$ bond angles for the (microcanonical) partition function of a system of K flexible polymers with ‘‘energy’’ f_F [48], i.e.,

$$\begin{aligned}\tilde{\Omega}_F(f_F,K,N,M,z)=&\left[\frac{1}{K!2^K}\frac{M!}{(M-KN)!}\left(\frac{z}{M}\right)^K\right.\\&\left.\times\left(\frac{z-1}{M}\right)^{K(N-2)}\right]\left[\binom{K(N-2)}{f_FK(N-2)}\right.\\&\times\left(\frac{1}{z-1}\right)^{(1-f_F)K(N-2)}\\&\left.\times\left(\frac{z-2}{z-1}\right)^{f_FK(N-2)}\right].\end{aligned} \tag{8}$$

In this equation the first factor is a mean-field approximation for K SAW-polymers (self-avoiding walk-polymers), each consisting of N monomers, on a lattice with M sites [46,47,50]. The second factor is a binomial distribution, yielding the probability that $f_FK(N-2)$ bond angles out of a total of $K(N-2)$ are flexed.

f_F has been defined as the probability of a flexed bond, modeling the transition to the nematic phase. Our model shows no nematic transition, but there is a parallel to the original work of Flory: Both models contain a two-level Hamiltonian. Since in our model the energy is rather connected with the bonds than with the bond angles, $(N-2)$ has to be replaced by $(N-1)$ in Eq. (8). We also change the notation from f_F to f to emphasize that in our work f is no measure of the flexibility any longer. Assuming that for a nonreversal random walk (NRRW) always one of the $(z-1)$ bonds has energy 0 instead of ϵ, it is

$$\begin{aligned}\Omega_F(f,K,N,M,z)=&\left[\frac{1}{K!2^K}\frac{M!}{(M-KN)!}\left(\frac{z}{M}\right)^K\left(\frac{z-1}{M}\right)^{K(N-2)}\right]\\&\times\left[\binom{K(N-1)}{fK(N-1)}\left(\frac{1}{z-1}\right)^{(1-f)K(N-1)}\right.\\&\left.\times\left(\frac{z-2}{z-1}\right)^{fk(N-1)}\right].\end{aligned} \tag{9}$$

Hence the microcanonical entropy is given by

$$\begin{aligned}s_F(f,K,N,M,z)&=\frac{1}{V}S_F(f,K,N,M,z)\\&=\frac{1}{V}\ln\Omega_F(f,K,N,M,z),\end{aligned} \tag{10}$$

where V is the volume of the system, which is given by $V=8(KN+H)$ (there are KN monomers and H holes, each occupying eight sites of the lattice). Since H depends on temperature, V has to be calculated for each temperature separately to ensure that the theory describes a melt at the same temperature and effective density as the simulation.

C. Milchev's criticism

Flory's result was criticized by Gujrati and Goldstein [51,52] and Milchev [53]. Here we follow Wittmann's exposition of Milchev's approach [46]. The criticism is that the number of free lattice sites accessible to a chain is not M but $M-(j-1)M/K$, if there are already $(j-1)$ chains on the lattice, since each chain consumes an average volume M/K. According to Milchev and Wittmann the first factor in Eq. (9) has to be modified

$$\frac{z}{M}\rightarrow\frac{z}{[1-(j-1)/K]M}=\frac{K}{K-(j-1)}\frac{z}{M}, \tag{11}$$

$$\frac{z-1}{M}\rightarrow\frac{z-1}{[1-(j-1)/K]M}=\frac{K}{K-(j-1)}\frac{z-1}{M}, \tag{12}$$

and thus

$$\begin{aligned}\left(\frac{z}{M}\right)^K\left(\frac{z-1}{M}\right)^{K(N-2)}&\rightarrow\left(\prod_{j=1}^{K}\frac{K}{K-(j-1)}\right)^{N-1}\\&\quad\times\left(\frac{z}{M}\right)^K\left(\frac{z-1}{M}\right)^{K(N-2)}\end{aligned} \tag{13}$$

$$=\left(\frac{K^K}{K!}\right)^{N-1}\left(\frac{z}{M}\right)^K\left(\frac{z-1}{M}\right)^{K(N-2)}. \tag{14}$$

With these substitutions a modified partition function results, which differs from Eq. (9) only by a constant prefactor

$$\Omega_M(f,K,N,M,z)=\left(\frac{K^K}{K!}\right)^{N-1}\Omega_F(f,K,N,M,z). \tag{15}$$

For large numbers like K Stirling's formula can be applied, i.e.,

$$\ln\left(\frac{K^K}{K!}\right)^{N-1} = (N-1)K, \tag{16}$$

yielding for the entropy

$$\begin{aligned} s_M(f,K,N,M,z) &= \frac{1}{V}\ln\Omega_M(f,K,N,M,z) \\ &= s_F(f,K,N,M,z) + \frac{K(N-1)}{V}. \end{aligned} \tag{17}$$

The entropies s_M and s_F differ only by a positive additive constant and so $s_M > s_F$. The discussion of Ref. [46] demonstrated that in the limit of the totally occupied lattice, $N \to \infty$ and $T \to 0$ s_M vanishes so that $s_F < 0$. This negative entropy was interpreted as evidence for a thermodynamic phase transition which occurs at a nonzero temperature T_2, where $s_F = 0$. On the other hand, in Milchev's treatment such a transition is clearly absent.

D. Gibbs-DiMarzio theory of a compressible polymer melt

The Gibbs-DiMarzio theory describes a compressible polymer melt [8–11]. With the help of Stirling's formula the corresponding partition function may be written as [46]

$$\begin{aligned} \Omega_{\mathrm{GDM}}(f,K,N,H,z) &= [(KN+H)z/2]^{K(N-1)} \\ &\quad \times \frac{[(K\tilde{N}+H)z/2]!}{[(KN+H)z/2]!} \\ &\quad \times \Omega_F(f,K,N,M,z), \end{aligned} \tag{18}$$

where the number of holes H (and thus the volume $M = KN + H$) is treated as a variable parameter, and $\tilde{N}z$ is the number of nearest neighbors of a rodlike polymer. The parameter $\tilde{N}$ is defined via [46]

$$\tilde{N} = 2\,\frac{z-1}{z} + (N-2)\,\frac{z-2}{z}. \tag{19}$$

Thus the entropy differs from the one calculated by Flory only by an additional term, giving an offset. However, in this case the offset depends on temperature.

Wittmann has shown [46] that the entropy of Gibbs-DiMarzio is given by

$$\frac{S_{\mathrm{GDM}}}{KN+H} = \frac{S_M}{KN+H} + \frac{z}{2}\left(\frac{K\tilde{N}+H}{KN+H}\right)\ln\left(\frac{K\tilde{N}+H}{KN+H}\right). \tag{20}$$

Since $\tilde{N} < N$, $\ln[(K\tilde{N}+H)/(KN+H)]$ becomes negative and we find $S_{\mathrm{GDM}} < S_M$. In the same limit, where S_M vanishes, S_{GDM} would thus become negative. The temperature where S_{GDM} becomes zero is then identified with the temperature of the underlying thermodynamic glass transition, arguing that S_{GDM} stays 0 is the glassy phase.

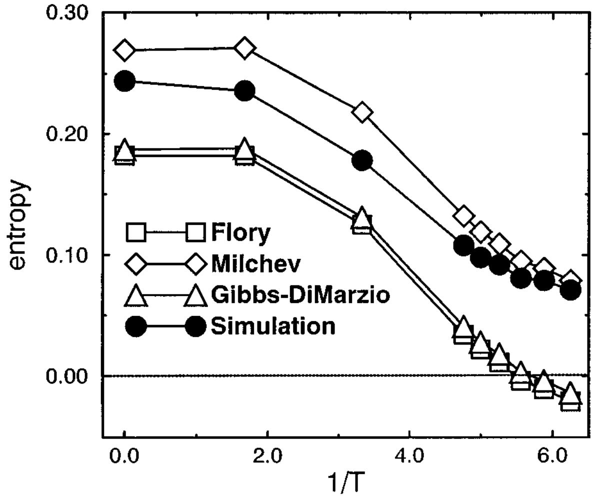

FIG. 6. The entropy per lattice site s vs the inverse temperature $\beta = 1/T$. The results of the simulation are compared with the original formulas (see text for details). s is measured in units of k_B.

E. Results

In this section the results of the simulation are compared with the formulas by Flory [Eq. (9)], Milchev [Eq. (15)], and Gibbs-DiMarzio [Eq. (18)]. For this comparison two strategies are followed: On the one hand, all input parameters, i.e., z, f, and H, are taken from the simulation, and on the other hand, one of them, i.e., z, is used as a free fit parameter.

Figure 6 depicts the results for the case, where all parameter were determined in the simulation (i.e., no parameter adjustment was done.). Flory's and Gibbs-DiMarzio's formulas exhibit a quite similar behavior. Both curves show that the entropy strictly decreases when the system is cooled down and becomes zero for $T \approx 0.18$ (Flory) and $T \approx 0.17$ (Gibbs-DiMarzio). These temperatures coincide within the error bars with the above mentioned estimate for the Vogel-Fulcher-temperature T_0 of the system. Unfortunately it cannot be decided if the entropy continues to fall for lower temperatures or adopts a constant value. It should be remarked that nearly the same results are obtained if H is not measured for each temperature, but always set to its athermal value. The effect of a variation of H on the entropy is therefore rather weak for the present model. However, this may be different in other systems. Therefore we use $H = H(T)$ in the following discussion to use a consistent interpretation of the theoretical parameters.

If the predictions of these theories are compared with the results of the simulation, some deviations are obvious. The entropy is underestimated by the theories. For high temperatures this is only a simple factor of about 1.3, but in the temperature range of the glass transition the qualitative behavior changes. The entropy from the simulation is still distinctly nonzero and decreases only by a factor of 3 when the melt is cooled from $T = \infty$ to T_g. Thus there is no evidence for a vanishing entropy.

Milchev's formula provides a somewhat better description of the simulation data. The theory predicts a strictly positive entropy over the whole range of temperatures. As the simulation data Milchev's entropy decreases by a factor of 3 with temperature, but a quantitative agreement cannot be ob-

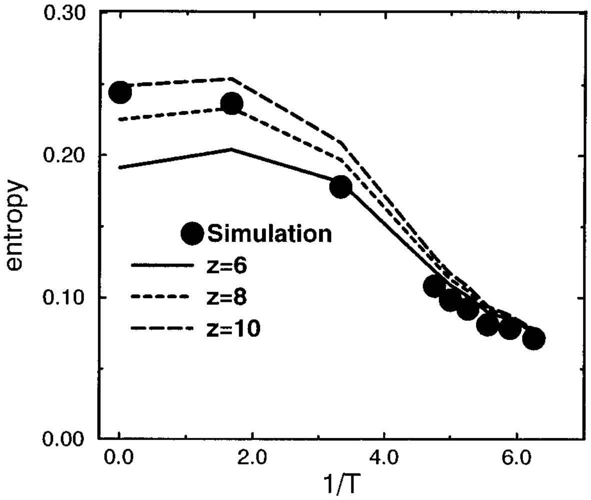

FIG. 7. Milchev's entropy per lattice site s_M vs the inverse temperature $\beta=1/T$ for different coordination numbers z which are treated as free parameters. s is measured in units of k_B.

tained. Equation (17) overestimates the entropy by about 10. . . 20%. The largest discrepancies occur at intermediate temperatures. However, one has to take into account that the theory treats the many-body interactions of a dense melt in a rather approximate fashion so that a perfect quantitative coincidence of simulation data and theoretical prediction should not be expected. A deviation of 10–20 % is therefore a rather satisfying result.

Based on this result one could try to improve the quantitative agreement between Milchev's theory and the simulation data by treating the coordination number as a free, temperature independent parameter, whereas f and H are taken from the simulation. Figure 7 shows for a few reasonable choices for the coordination number that there is no value of z which describes the data over the whole temperature range. In the low temperature region the curves for all z values coincide and always overestimate the simulated entropy. If the temperature increases, the curves start to splay out, remaining either entirely above the simulation data, coinciding with them at high temperatures, or crossing them at intermediate temperatures, depending on the choice of z. Therefore Eq. (17) with a constant z value worsens the qualitative agreement between theory and simulation and is thus not a competitive alternative to the description with temperature dependent coordination number.

F. Adam-Gibbs relation

In the Adam-Gibbs theory the entropy determines the diffusion constant of the melt by the relation [3,54]

$$D(T)=D(\infty)\exp\left(-\frac{A}{TS}\right). \tag{21}$$

$D(\infty)$ is easily obtained from g_3 (defined as the mean-square displacement of the center of mass of the chains) via

$$D(\infty)=\lim_{t\to\infty}\frac{g_3}{6t}\approx 5.2\times 10^{-4}. \tag{22}$$

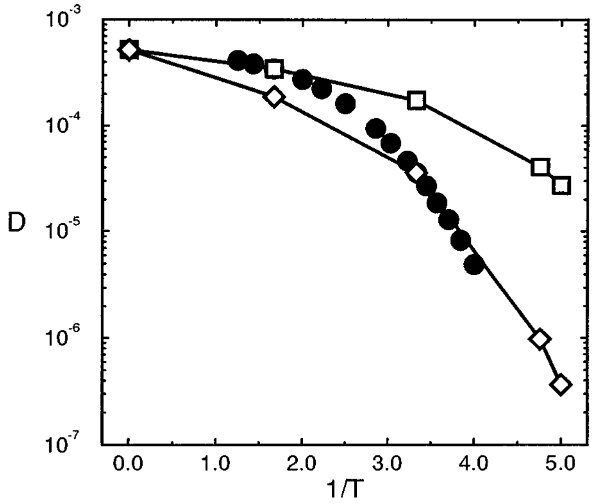

FIG. 8. The diffusion constant D vs the inverse temperature $\beta=1/T$. The filled circles are a direct measurement (from [34]), ''◇'' is the Adam-Gibbs relation with $A=0.0581$, and ''□'' with $A=0.143$ (see text for details). D is measured in units of a^2 per Monte Carlo step where a is the lattice constant.

A is a fit parameter. The theoretical predictions are compared with the above mentioned results for the diffusion coefficient [34] and should be determined via Eq. (21) for $T\geqslant 0.25$.

Figure 8 compares the direct measurement of D with theoretical predictions with two different values of A. Though the shape of the theoretical and the measured curve is similar, the quantitative agreement is rather poor. We have chosen two typical values for A. Theory and simulation always agree at one temperature, while the theory overrates D for lower and underrates it for higher temperatures. To obtain coincidence between the Adam-Gibbs relation and the simulation data at high temperatures, A has to be set to 0.0581, giving the upper curve. To achieve the same at lower temperatures, A has to be set to 0.143, giving the lower curve. These two curves define the range, in which A can be varied. It is not possible to choose a value of A that predicts the diffusion constant correctly over a whole temperature range. However, this test of the Adam-Gibbs theory is only preliminary, since there are only two data points for the entropy in the temperature interval, where the diffusion coefficient decreases strongly (i.e., for $T\leqslant 0.6$) and where we would expect Eq. (21) to hold.

IV. DISCUSSION

We have measured the entropy of the polymer melt in a computer simulation. Since we have used a fast ''slithering-snake'' algorithm [36], we are sure that the data do not contain nonequilibrium effects. This set of data allows a test of theoretical predictions for the entropy even in the temperature range close to the glass transition. The strictly positive entropy over the whole range of temperatures is a first indication that the theories of Flory and Gibbs-DiMarzio cannot predict the entropy accurately. The usual interpretation, that the experimentally observed glass transition signifies the vanishing of the configurational entropy at a finite temperature in the hypothetical limit of quasistatic cooling, is therefore questionable.

Nevertheless there are important insights in the transition to the glassy phase. We can conclude that the entropy is described over the whole range of temperatures from $T=\infty$ to T_0 by *one* formula. This even holds for the temperature range where the theory predicts a phase transition and demands that the entropy is set to 0 instead of the value predicted by the formula. In contrast to that the entropy is always *strictly positive*, even below the temperature where the glass transition occurs. The entropy catastrophe predicted by Flory for the limit of the low temperature and a fully occupied lattice is removed by Milchev's extension. It is interesting to note that the entropy catastrophe, produced by the formulas of Flory and Gibbs-DiMarzio, occurs at a temperature that coincides with the Vogel-Fulcher temperature of our system within the estimated errors.

The basic difference of the calculations of Flory, Gibbs-DiMarzio, and Milchev lies in the approximation of the translational part of the partition function. This leads to the underestimation of the entropy already in the high temperature limit. The intramolecular part with its dependence of the energy parameters is the same in all three theories leading to the same shape of the predicted curves as a function of temperature. Since the shape of the entropy vs temperature curve is correctly reproduced, predictions for experimental quantities like the specific heat will still be in good agreement with the experimental findings. Thus the theories are useful to analyze experiments but the intimate connection of the experimental glass transition at T_g and a thermodynamic phase transition at $0<T_2<T_g$ is not stringent.

ACKNOWLEDGMENTS

We would like to thank H. P. Wittmann and M. Müller for helpful discussions. We are very grateful to the Höchstleistungsrechenzentrum (HLRZ) at Jülich and to the Regionales Hochschulrechenzentrum Kaiserslautern (RHRK) for a generous grant of computer time on the CRAY-YMP. This work was supported by the Deutsche Forschungsgemeinschaft (SFB 262).

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