Bethe-Peierls Approximation for Linear Monodisperse Polymers
Re-examined

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Abstract

Bethe-Peierls approximation, as it applies to the thermodynamics of polymer melts, is reviewed. We compare the computed configurational entropy of monodisperse linear polymer melt with Monte Carlo data available in literature. An estimation of the configurational contribution to the total liquid’s Cp is presented. We also discuss the relation between Kauzmann paradox and polymer semiflexibility.

1 Introduction

In 1948, Kauzmann [1] recognized a peculiar fact about the thermodynamic behavior of liquids in the vicinity of glass transition. The configurational entropy of supercooled liquids drops very rapidly with temperature decrease and this leads to the entropy crisis. It looks like the entropy would drop to zero at $T > 0$ and then something should happen to the system in order to avoid the entropy becoming negative. The problem has attracted much theoretical attention after the work by Gibbs and Di Marzio [2]. They demonstrated, by means of a statistical calculation, that the entropy of a disordered polymer liquid extrapolates to negative values at low temperatures. This entropy crisis violates the Nernst postulate and makes the problem very puzzling. To resolve this problem, they proposed that the second-order transition to a unique state, the ideal glass, would occur at the temperature where the configurational entropy turns to zero. Gujrati and Goldstein [3, 4] criticized the Gibbs-DiMarzio theory for the absence of a crystalline state. The crystal to liquid states and their metastable extensions in a polymer system were subsequently captured by Corsi and Gujrati [5, 6] with a demonstration of the configurational entropy crisis at low temperatures for the metastable liquid state. They pointed out that the unusual ideal-glass transition in the metastable region does not violate the thermodynamic laws provided that the stable crystalline state exists below the melting temperature, $T_M > T_K$, see also [7]. In addition, developed by Freed and co-workers [8] the lattice cluster theory predicts that the configurational entropy would extrapolate to zero at a positive temperature [9], as in the Gibbs-DiMarzio theory.

The present work concerns only the equilibrium melt of monodisperse polymers, whereas the equilibrium polymerization requires additional parameters, e.g. polymer polydispersity. Monodisperse polymers can be prepared in laboratory and, more importantly, can be simulated using Monte Carlo methods. In the present work, the crystal is not captured, even though it is possible to construct such a state for monodisperse polymers. Strictly speaking, the total configurational entropy is the sum over the entire energy spectrum. However, crystal, glass and liquid states are usually pictured to occupy separate basins of the energy landscape [10], which suggests that the corresponding systems can be treated separately. It is important to understand whether or not matter could exist in a form of a deeply supercooled liquid, even though the configurational entropy of glass may dif-
fer form that of the liquid at the same temperature [11, 12, 13].

In an attempt to address to this problem, an analytic calculation of configurational entropy of a polymer melt is presented in order to provide a framework for a more systematic study. To solve the problem we use the Bethe-Peierls approximation, which is a lattice gas theory neglecting all closed loops of the regular lattice. More precisely, we want to investigate the interplay of the effects due to closed loops of a regular lattice, polymer chain length and chain semiflexibility, and to relate this to the entropy crisis.

2 Model

We consider the semiflexible linear polymers of the same length \( x \) distributed on the lattice. The penalty for a chain bend is introduced by means of the Flory’s flexibility [20, 21], \( f \). The interactions among monomers are taken into account by assigning the energy, \( V < 0 \) (attractive interaction), to the nearest-neighbor pairs of occupied sites. The Bethe-Peierls approximation [22, 23] was originally developed for single site species. Later, Chang [24] applied the method to diatomic molecules. The aim of the present paper is to extend the Chang’s method to polyatomic species. The entropy expression is found to reduce to the Flory-Huggins form [25, 26] in the appropriate limit: \( V \to 0 \) and \( z \to \infty \), provided that \( zV=\text{const} \), where \( z \) is the lattice coordination number.

3 Bethe-Peierls approximation

The main idea of the method is to calculate the grand partition function (GPF) for configurations of an aggregate composed of a molecule occupying a lattice site (internal site) and its \( z \) neighbors (surface sites) in the framework of a mean-field theory: An effective field is superimposed on the surface molecules by molecules outside the aggregate. It is determined making use of the condition of equal probability for the internal molecule as well as for any molecule from the aggregate surface to be in a particular configuration. After determination of GPF other quantities such as energy (enthalpy at constant pressure), specific heat, etc. follow at once.

The effective interaction parameter, \( V \), is defined as the energy of interaction between two occupied sites that are nearest-neighbors to each other irrespective of whether they are connected by a bond or not. To account for presence of free volume, the lattice-hole model is employed in which both monomers and holes (empty lattice sites) populate a lattice with the occupancy controlled by the system chemical potential, \( \mu \). The polymer semiflexibility is incorporated through \( U_f \) being the energetic penalty for creation of a chain bend. Based on this information, a general form of GPF can be given:

\[
Z = \sum \Omega(n, X, N, N_g) \eta^X \lambda^N w_f^{N_g}, \tag{1}
\]

where \( \eta = \exp(-V/k_B T) \) is the Boltzmann weight for the interactions between occupied sites, \( \lambda = \exp(\mu/k_B T) \) is the absolute activity, \( w_f = \exp(-U_f/k_B T) \) is the Boltzmann weight for the flex energy, \( n \) is the total number of occupied sites, \( X \) is the number of nearest-neighbor pairs of occupied sites, \( N_g \) is the total number of the gauche configurations, \( \Omega \) is the number of arrangements on a lattice of \( N \) sites that have the same numbers of \( n, X, \) and \( N_g \).

For comparison purposes, it is instructive to begin by presenting the original Bethe-Peierls technique. Next, we are going to present a modification due to the chain connectivity. At first, the aggregate is pictured as a site surrounded by \( z \) surface sites. A set of numbers is defined: \( \{ \theta_i \} = \theta_0, \theta_1, ..., \theta_z \), which are 0 or 1 according as the corresponding sites are empty or occupied, where the index \( i = 0 \) is reserved for the internal site. A configuration with the internal site being unoccupied \( (0; \theta_1, ..., \theta_z) \) contributes to GPF as the sum over all arrangements on the surface sites

\[
\sum_{\{ \theta_i \}} \lambda^{\theta_1 + ... + \theta_z} \psi(\theta_1, ..., \theta_z), \tag{2}
\]

where \( \psi \) is the field that couples the aggregate configurations to the external distribution. Presuming that there are no sites occupied by the segments of the same chain among the surface sites, two types of
correlations generated by a local configuration can be identified: the occupancy of a surface site 1) means the possibility of the bond presence between the given site and an external nearest-neighbor site, 2) induces the mer-mer interaction with the occupied external sites. An empty surface site does not induce any correlations to the exterior. These facts can be generally taken into account presuming that \( \psi \) is given by

\[
\psi = c^{\theta_1 + \ldots + \theta_z},
\]

where \( c \) is some constant. From this follows that for the configuration \((0; \theta_1, ..., \theta_z)\) GPF is given by

\[
\sum_{\{\theta_i\}} c(\lambda \xi)^{\theta_1 + \ldots + \theta_z} = c(1 + \lambda \xi)^z.
\]

To study the linear chains, we consider the aggregate composed of \( x \) sites and their \( x \) nearest neighbors. The modification was inspired by the papers published quite some time ago [24, 27, 28]. The GPF for the configuration \((1, ..., 1; \theta_{x+1}, ..., \theta_{x+z})\) can be represented in the following general form:

\[
\sum_{i=1}^{z} \sum_{\{\theta_j\}} c_x \lambda^{x-1} \eta^{x-1} (\lambda \eta \xi_x)^{x-\theta_j + \ldots + \theta_z},
\]

where \( z \) is an over configurations permitted by the linear chain topology, the second sum is over configurations on the surface sites, the factor \( \eta^{x-1} \) takes into account the interactions among the segments of the chain inside the aggregate, and

\[
\sum_j \theta_j = \theta_1 + \ldots + \theta_{j-1} + \theta_{j+1} + \theta_z.
\]

In order to calculate \( \chi_k \), we propose a recursive method analogous to the Cayley tree technique [29]. Accordingly, the aggregate composed of a site and its \( z \) neighboring sites corresponds to the center of the Cayley tree. As before, the configurations with the central site being unoccupied are included in GPF by the term \( c(1 + \lambda \xi)^z \), where \( \xi \) represents the effective field for the case when no bond is present inside the aggregate. For the case when the central site is occupied by an end-point or by a middle group, we define \( \chi_k \) to account for correlations induced on the aggregate due connectivity of the chain; where \( k \) is the number of bonds in the chain piece extending beyond the surface site of the aggregate. The GPF can be formulated as follows:

\[
Z = c(1 + \lambda \xi)^z + cz(1 + \lambda \eta \xi)^{z-1} \lambda^2 \eta \chi_{x-1} + \frac{cz^2}{2} r_f (1 + \lambda \eta \xi)^{z-2} \lambda^3 \eta^2 \sum_{k=1}^{x-2} \chi_k \chi_{x-k-2},
\]

where the factor \( z \) in the second term is the number of orientations for the bond extending from the endpoint occupying the internal site of the aggregate; in the third term, the factor

\[
r_f = w_f (z - 2) + 1
\]

takes into account the semiflexibility. The latter is derived making use of the assumption that the number of trans configurations in the aggregate is equal to \( z/2 \). In the case when \( z \) is an even number and the surface sites, situated around the internal (central) site, are equally spaced, \( z/2 \) is easily identified as the number configurations of two bonds with the 180 degree angle between them. Note that this simplified picture does not apply when \( z \) is an odd number since a construction of trans configurations with the 180 degree angle between the bonds is not possible for this case. Proceeding further with our description of \( \chi_k \), we justify the statistical weight \( z r_f / 2 \) by means of the relation

\[
\left[ \frac{z(z - 1)}{2} - \frac{z}{2} \right] w_f + \frac{z}{2} = \frac{z}{2} r_f,
\]

where \( z(z - 1)/2 \) is the total number of configurations for two bonds inside the aggregate. In order to evaluate GPF, we obtain the Bethe lattice recursive relations for \( \chi_k \):

\[
\begin{align*}
\chi_1 &= \epsilon' (1 + \lambda \eta \xi)^{z-1}, \\
\chi_2 &= \epsilon' r_f \lambda \eta (1 + \lambda \eta \xi)^{z-2} \chi_1, \\
&\vdots \\
\chi_k &= \epsilon' r_f \lambda \eta (1 + \lambda \eta \xi)^{z-2} \chi_{k-1},
\end{align*}
\]

where the factor \( r_f \) and the power \( z - 2 \) are due to the fact that there are \( z - 2 \) local gauche conformations.
out of \( z - 1 \) possible for a middle segment located anywhere except the center of the Cayley tree, \( c' \) is a scaling factor measuring the distance from the Cayley tree center to be evaluated in the following. The summation in the third term of (7) can now be carried out to yield

\[
\sum_{k=2}^{x-1} \lambda^k \chi_{x-k-2} = (x-2)(c' r f \lambda \eta)^x - 3(1 + \lambda \eta \xi^{(z-3)(z-2)})^2
\]

(11)

Finally, we find

\[
Z = c(1 + \lambda \xi)^x + c c' \chi x \lambda^x \eta^x - 1(1 + \lambda \eta \xi)^x c'
\]

(12)

where \( \gamma \) is the number of ways per site the polymer chain can be arranged on otherwise empty lattice. We find that \( \gamma_{\text{flex}} = \frac{1}{2} (z - 1)^x - 1 \) for completely flexible chains, \( \gamma_{\text{rigid}} = \frac{1}{2} \) for rigid rods, and \( \gamma_{\text{semiflexible}} = \frac{1}{2} (w f (z - 2) + 1) \) for semiflexible chains. The GPF for this configuration will be

\[
c x \gamma x \lambda^x \eta^x - 1(1 + \lambda \eta \xi)^x c'
\]

(13)

where \( c_x \) and \( \xi_x \) can be related to \( c \) and \( \xi \), respectively: We write GPF for the aggregate with the empty internal site and one empty surface site, and compare it with GPF written for the aggregate with two empty sites being internal. The former is obtained summing over all \( \theta \)'s on \( z - 1 \) surface sites, which results \( \sum_{\{ \theta_i \}} c(\lambda \xi)^{\theta_x + \ldots + \theta_z} \). The latter is evaluated by summing over \( 2(z - 1) \) surface sites:

\[
\sum_{\{ \theta_i, \theta_j \}} c(\lambda \xi)^{\theta_x + \ldots + \theta_z + \theta'_x + \ldots + \theta'_z}.
\]

(15)

Both partition functions should be the same, hence the relations \( \xi = \xi_2 \) and \( c = c_2(1 + \lambda \xi)^{z-1} \) are valid, as found by performing the summation over various configurations \( \theta'_2, \ldots, \theta'_z \). This idea can be applied for aggregates of larger sizes. Our suggestion: since the chains consist of \( x - 1 \) bonds each, the relation should be

\[
\xi = \xi_x \quad \text{and} \quad c = c_x(1 + \lambda \xi)^{(z-1)(z-1)},
\]

(16)

which yields

\[
Z = c(1 + \lambda \xi)^x + c x \gamma x \lambda^x \eta^x - 1(1 + \lambda \eta \xi)^x
\]

(17)

which is identical to (12) provided \( c' = (1 + \lambda \xi)^{(z-1)} \).

Having established GPF, we now turn to the detailed study of the equal probability condition for absorption at the internal site and surface sites. Note also that this probability is the fractional coverage of the lattice \( \theta = n/N \). The following pair of equations

\[
\theta = (z Z)^{-1} \sum_{i_2 i_3 \ldots i_{\Sigma}} c_x \lambda^x \eta^x - 1(1 + \lambda \eta \xi)^x
\]

(18)

\[
\theta = (z Z)^{-1} c \sum_{\{ \theta_i \}} (\theta_1 + \ldots + \theta_x) (\lambda \xi)^{\theta_1 + \ldots + \theta_x}
\]

and

\[
(x Z)^{-1} c (1 + \lambda \xi)^x + (z Z)^{-1} c x \gamma x \lambda^x \eta^x - 1
\]

\[
\times (2 (x - 1) (1 + \lambda \eta \xi)^{x'} + \xi \frac{\partial}{\partial \xi} (1 + \lambda \eta \xi)^{x'})
\]

are obtained in analogy with the corresponding equations from Ref. [24]. Combining Eqs. (18) and (19), one finds the equations of state:

\[
\frac{\theta}{1 - \theta} = \frac{x z \xi (1 + \eta \xi)}{z' + 1 + \varepsilon}
\]

(20)

\[
\gamma \lambda^x \eta^x - 1 \lambda^x = \frac{x \varepsilon (1 + \varepsilon) x^2 + z'}{z' + (1 + \eta \xi)^{x' - 1}}
\]

(21)

where \( \varepsilon = \lambda \xi \). The solution of the quadratic equation (20) is given by

\[
\varepsilon(\theta) = \varepsilon_+ = \frac{\theta z - (1 - \theta) x z + D}{2 z x \eta (1 - \theta)}
\]

(22)

where

\[
D = \sqrt{[\theta z - (1 - \theta) x]^2 + 4 z' x \eta \theta (1 - \theta)}
\]

(23)
Another solution with the negative sign before \( D \) in \((22)\) is physically irrelevant, since \( \varepsilon_- = -1 \) in the athermal limit \( \eta = 1 \), while \( \varepsilon_+ = z'\theta/z(1 - \theta) > 0 \) in this case.

There is another method to derive \((20)\) and \((21)\): The occupation \( \theta \) is obtained as the ratio of the term corresponding to the occupied internal site to the total partition function:

\[
\theta = \frac{Z^{-1}c\xi Z^{-2}x\lambda \eta^{z-1}(1 + \lambda \xi)^{-1(x-1)(z-1)}(1 + \lambda \eta \xi)^{z'}}{1 - \theta}.
\]

This allows us to derive \((21)\):

\[
\frac{z^2 \phi - 2z + x \lambda \eta \xi^2}{2} = \frac{\lambda \xi}{\lambda \eta \xi} = \frac{\theta}{1 - \theta} \frac{(1 + \lambda \xi)^{x-1} + \lambda \eta \xi^{z-1}}{(1 + \lambda \eta \xi)^{z'}}.
\]

(25)

It should also be considered that the probability to find the internal site of the aggregate unoccupied can be calculated by two methods:

\[
Z^{-1}c(1 + \lambda \xi)^z
\]

and

\[
Z^{-1}c\{(1 + \lambda \xi)^{z-1} + (z - 1)\lambda \eta(1 + \lambda \eta \xi)^{z-2} \chi_{x-1} + \frac{z - 2}{2} \phi(1 + \lambda \eta \xi)^{-1} \chi_{z-2} \}
\]

(27)

where the quantity in the curly brackets is the partial partition function for the surface \( z \) sites calculated under the condition that the internal site is empty. Thus, with aid of \((25)\), we obtain

\[
(1 + \lambda \xi)^z = (1 + \lambda \xi)^{z-1} + \frac{z' \theta}{z x} \frac{(1 + \lambda \xi)^z}{1 - \theta (1 + \lambda \eta \xi)},
\]

(28)

which can be reduced to \((20)\).

To this end we remark that one can also derive these equations solely from the kinetic considerations for molecular absorption/desorption process \([30]\). Here we provide only the derivation of the first equation to save space. In the aggregate represented by a site surrounded by \( z \) sites, the probability for a configuration \((0; \theta_1, \ldots, \theta_z)\) to occur is assumed to be proportional to \( \phi^{\theta_1 + \ldots + \theta_z} \), where \( \phi \) is the quantity to be determined further. Then, the probability for the internal site to be unoccupied should be proportional to \( \sum\phi^{\theta_1 + \ldots + \theta_z} = (1 + \phi)^z \). Hence, the probability for one of its \( z \) neighbors to be occupied is given by

\[
\sum \phi^{\theta_1 + \ldots + \theta_z} = \phi(1 + \phi)^{z-1} = \frac{\phi}{1 + \phi}.
\]

(29)

For the aggregate enclosing a chain with its neighborhood, the probability for any of the surface sites to be occupied, provided all internal sites are empty, is calculated in the analogous manner and is given by

\[
\frac{\phi}{1 + \phi},
\]

(30)

where \( \phi \) is the quantity similar in nature to \( \phi \). Comparing \((29)\) and \((30)\), one gets \( \phi = \phi \). The probabilities for various states of occupation of the surface sites, provided that all \( z \) internal sites are occupied, are proportional to \( (\eta \xi)^{\theta_1 + \ldots + \theta_z + \frac{z'}{2}} \), which gives

\[
\frac{\eta \phi}{1 + \eta \phi}
\]

(31)

for the probability of a surface site to be occupied when the internal sites are also occupied. The condition is

\[
\theta = (1 - \theta) \frac{\phi}{1 + \phi} + \frac{2(x - 1)}{z x} \frac{z' \eta \phi}{z x \ln 1 + \eta \phi},
\]

(32)

where \( \frac{2(x - 1)}{z x} \theta \) is the ratio of number of bonds \( 2(x - 1) \theta / z x \) per lattice site to the total number of lattice bonds \( z / 2 \) per lattice site representing the probability to have a bond extending from an occupied site. The equation \((20)\) follows immediately taking

\[
\phi = \varepsilon.
\]

(34)

4 Thermodynamics

Further analysis of \((11)\) can be carried out to derive the configurational entropy expression. First, we write the partition as

\[
Z = \sum \Omega \lambda \eta^x w_f^N
\]

(35)

and

\[
= \sum e^{N(\theta_2(\phi) + \theta_2 \ln \lambda + \theta_2 \ln \eta + \theta_2 \ln w_f)},
\]

(36)
where \( \theta_X = X/N \), and \( \theta_g = N_g/N \). The minimal free energy can by achieved applying the condition:

\[
\frac{\partial}{\partial \theta} [\theta g(\theta) + \theta \ln \lambda + \theta_X \ln \eta + \theta_g \ln w_f] = 0. \quad (37)
\]

Thus, the configurational entropy is given by

\[
S_N/k_B = [\theta g(\theta)]^* = - \int \ln \lambda d\theta - \theta_X \ln \eta - \theta_g \ln w_f, \quad (38)
\]

where \( S_N \) is the entropy per lattice site. Note, \( g^*(0) = 0, \theta_X(0) = 0, \) and \( \theta_g(0) = 0 \). It is appropriate to define the entropy per monomer:

\[
S_n = S_N/\theta. \quad (39)
\]

After integration of (38), the entropy expression adopts the form

\[
S_n/k_B = \frac{1}{x} \ln(\gamma x \eta^{x-1}) - \frac{1}{x} \ln \theta - \frac{(1 - \theta)}{\theta} \ln(1 - \theta) + \frac{(x - 1)(1 - \theta)}{x \theta} \ln[(1 + \varepsilon)(1 - \theta)] + \frac{z' \ln \theta + z' (1 - \theta) \ln(1 - \theta)}{x} + \frac{z' \ln(\frac{z x}{z'}) + z' \ln(\frac{1 + \varepsilon}{1 - \theta})}{2 \theta} + E_n/k_B T,
\]

where \( E_n/k_B T = - (\theta_X \ln \eta + \theta_g \ln w_f)/\theta \) is the system internal energy per monomer.

The contact density \( \theta_X \) is evaluated making use of the lattice topological relations:

\[
\begin{align*}
\theta X &= 2\theta X + \theta X' , \quad (41) \\
\theta X(1 - \theta) &= 2\theta X' + \theta X'' , \quad (42)
\end{align*}
\]

where \( \theta X' \) is the density of pairs formed by an empty site adjacent to an occupied and \( \theta X'' \) is the density of nearest-neighbor pairs formed by empty sites. We calculate \( \theta X'' \) from the fact that the probability of having an empty site being a neighbor to another empty site is, in accordance with (29), equal to \( 1/(1 + \varepsilon) \), and taking into account that there are on average \( z/2 \) lattice bonds per site:

\[
\theta X'' = \frac{z (1 - \theta)}{2} \frac{1 + \varepsilon}{1 + \varepsilon}. \quad (43)
\]

Then, we have

\[
\theta_X = z \theta - \frac{z}{2} \frac{1 + \theta}{2} \frac{1 + \varepsilon}{1 + \varepsilon}. \quad (44)
\]

The density of the gauche bonds \( \theta_g \) is given by

\[
\theta_g = \frac{\theta}{x} (x - 2) \frac{(z - 2) w_f}{1 + (z - 2) w_f}, \quad (45)
\]

where \( x/\theta \) is the number of polymers, \( (x - 2) \) is the number of middle groups in each polymer, and the factor

\[
f = (z - 2) w_f/[1 + (z - 2) w_f] \quad (46)
\]

is the probability to form the gauche configuration derived by Flory [20]. The latter can be obtained from our theory as well: The density of gauche bonds \( \theta_g \) is the ratio of

\[
\frac{z(1 - \varepsilon)}{2} - \frac{z}{2} = \frac{z(2 - \varepsilon)}{2} \quad (47)
\]

terms corresponding to the gauche configurations in (7) to the total GPF:

\[
\theta_g = \theta \frac{x - 2}{x} \frac{w_f}{r_f}, \quad (49)
\]

This completes our proof of (45).

The equilibrium properties of the system can be deduced from the thermodynamic identity

\[
\mu = H_n - T S_n, \quad (50)
\]

where the configurational enthalpy per monomer, \( H_n = \mu + P v_0/\theta \), with \( v_0 \) being the volume of a lattice site. By aid of Eq. (21) the density dependence of the chemical potential, \( \mu = k_B T \ln \lambda \), arises straightforwardly:

\[
\mu = - \frac{k_B T}{x} \ln(\gamma x \eta^{x-1}) + \frac{k_B T}{x} \ln\left(\frac{\theta}{1 - \theta}\right) (51)
\]

\[
+ \frac{k_B T}{x} (x - 1) \ln(1 + \varepsilon) + z' \ln\left(\frac{1 + \varepsilon}{1 + \eta \varepsilon}\right).
\]
Performing further algebraic manipulations, we derive

\[ P v_0 / k_B T = \frac{z}{2} \ln(1 + \varepsilon) + \frac{z - 2}{2} \ln(1 - \theta). \]  
(52)

The equation (52) serves as the implicit equation for determination of \( \theta \).

Making use of the relations for the densities, Eq. (40) can be written in a slightly different form

\[
\frac{S_n}{k_B} = \frac{1}{x} \ln \frac{z}{2} + \frac{\ln x}{x} - \frac{1}{\theta} \left( \ln(1 - \theta) + \frac{x - 1}{x} \ln(1 + \varepsilon)(1 - \theta) \right) + \frac{z'}{x} \ln \theta + \frac{z'(1 - \theta)}{\theta} \ln(1 - \theta) 
\]
\[
- \frac{z'}{x} \ln \left( \frac{x \varepsilon}{z'} \right) + \frac{z'}{x} \ln \left( \frac{1 + \varepsilon}{1 - \theta} \right) - \frac{(\theta_N - \theta_b) \ln \eta}{\theta} 
\]
\[
- \frac{x - 2}{x} \left[ f \ln f + (1 - f) \ln(1 - f) - f \ln(z - 2) \right],
\]

where \( \theta_b \) is the bond density given by \( \theta_b = (x - 1) / x \).

The equations (52) and (22) are to be solved numerically for \( \theta \) as a function of \( T \) at constant \( P \). We then substitute \( \theta \) and \( \varepsilon(\theta) \) calculated from (22) into (53) to obtain the entropy at a constant pressure. Finally, configurational heat capacity per occupied site, \( C_p \), can be computed from

\[ C_p = \left( \frac{\partial H_n}{\partial T} \right)_P, \]  
(54)

or equally from

\[ C_p = T \left( \frac{\partial S_n}{\partial T} \right)_P. \]  
(55)

According to our numerical computation, both equations give identical specific heat values.

5 Comparison with Other Results

In the present section, we analyze the main characteristics of the thermodynamic functions (52) and (53) in comparison with data available from experiments and simulations.

Presented as early as in 1976, the lattice fluid (LF) theory developed by Sanchez and Lacombe [31, 32], due to its simplicity and high level of prediction, became a foundation of many successional theoretical and experimental investigations of polymer systems [33]. In analogy with LF theory, the equation of state (52) can be written in terms of the reduced temperature \( T^* = -\frac{2k_B T}{zV} \) and pressure \( P^* = -\frac{2v_0 P}{zV} \). Figure 1 shows the experimental data for density, \( \theta \), vs. reduced temperature, \( T^* \), obtained from in Fig. 3 of Ref. [34] for various liquids. The line is the theoretical isobar \( (P^* = 0.25) \) computed applying the limit \( x \to \infty \) for \( z = 20 \).

Based on this we conclude that the present theory adequately describes the relationship of density, temperature, and pressure for pure polymer fluid.

The important difference between the theory by Sanchez and Lacombe and the present theory is in entropy. The LF entropy is independent of temperature, \( T \), vs. reduced temperature, \( T^* \), obtained from in Fig. 3 of Ref. [34] for various liquids. The line is the theoretical isobar \( (P^* = 0.25) \) computed applying the limit \( x \to \infty \) for \( z = 20 \). Based on this we conclude that the present theory adequately describes the relationship of density, temperature, and pressure for pure polymer fluid.

The important difference between the theory by Sanchez and Lacombe and the present theory is in entropy. The LF entropy is independent of temperature, while (53) exhibits a temperature dependence. This is a consequence of consideration of the con-
figurational distribution of the polymer system influenced by mer-mer interaction energy and polymer semiflexibility, which is absent in LF theory.

Recently, Davila et al. [14] presented Monte Carlo (MC) data for interacting dimers occupying one-dimensional, square, triangular and hexagonal lattice. Our configurational entropy expression (53), with an appropriate integer value for $z$, is in perfect agreement with the quasi-chemical approximation. In particular, Bethe-Peierls approximation becomes exact in the case of dimers on the one-dimensional lattice, see Fig. 2. Essentially, this is a numerical verification of the fact known to Chang [24]. The test of the present theory against the MC data shows a significant improvement over the Brag-Williams approximation. In addition, it shows some special features such as correspondence between $z$ and the coordination number of the regular lattice, i.e. $z = 2, 3, 4, 6$ for one-dimensional, honeycomb, square and triangular lattice, respectively. Chemical and physical topology of the adsorbing surface is known [15, 16] to be critically important for the adsorption ability of the surface. This local surface inhomogeneity may be attributed to an inhomogeneity of $z$ and could be treated using the recursive lattice approach as well [17, 18, 19].

### 6 Specific Heat

One of applications of this theory could be a comparison with experimental results available from literature for specific heat dependence on molecular weight and temperature. The specific heat of linear $n$-alkanes as a function of the number of carbons in the backbone is found to be a monotonically decreasing function [36, 37], while the specific heat of a continuously polymerizing system was measured to pass through a maximum [38]. We suggest that the controversy can be resolved in the framework of the present theory by studying the configurational specific heat as a function of chain length. Figure 3 shows $C_p$ vs. $x$ in three cases: $T^*_f = 0.48, 0.47, 0.46$ represented by continuous, dashed, and dotted lines, respectively; in all three cases $T^*_f = 0.5$, where
\( T^*_f \equiv zU_f/2 \). By showing this we want to demonstrate three types of typical behavior: for high temperatures \((T^* = 0.48 \text{ and above})\) the curve is always sharply decreasing, then reaching a constant value; for low temperatures \((T^* = 0.46 \text{ and below})\) the curve is monotonically increasing; in the intermediate region, the curve initially decreases reaches a minimum and then increases. As was shown by Di Marzio and Dowell \cite{39}, the specific heat has a large vibrational part, hence the above experimental results cannot directly be fitted by the theoretical curves at current stage. However, Johari et al. \cite{40, 41, 42} found experimentally that the vibrational specific heat of glass and liquid are practically the same. Accordingly, the configurational specific heat is useful for estimating the jump in heat capacity at the glass transition, provided the specific heat of glass is measured.

7 Discussion and Conclusion

We provide a very careful derivation of the entropy and the pressure expressions based on the Bethe-Peierls approximation for linear monodisperse polymer. The prediction of the system density at a given reduced pressure and temperature is shown to be in quantitative agreement the experimental data and with Monte Carlo simulations on square lattice. The overall configurational entropy of the polymer fluid consists of three fundamentally different types of contributions, i.e., the athermal entropy (translational and configurational degrees of freedom), the semiflexibility correction entropy, and the thermal correction entropy that is due to the thermal correction term of the partition function. The third type, that is absent in Flory-Huggins theory and LF theory by Sanchez and Lacombe, contributes the main part at low temperatures. We also demonstrate that our theory is equivalent to the Ryu-Gujrati theory with the correction due to chain semiflexibility.

We obtain the negative entropy states at certain conditions: low temperatures, \( T \subset [0..T_K] \), and some fixed pressure; high pressures, \( P \subset [P_K..\infty) \), and a fixed temperature; high molecular weights, \( x \subset [x_K..\infty) \), while both temperature and pressure are kept constant. These results are in qualitative agreement with the earlier work by Di Marzio et al. \cite{2, 35}. The entropy crisis was captured at low temperatures comparable to energy due to polymer semiflexibility. This indicates that the local anisotropy due to semiflexibility could be the route cause of entropy crisis in our calculation.

Our computation of the configurational specific heat as a function of chain length revealed that this function is monotonically increasing at low temperatures and monotonically decreasing at high temperatures. In the transition region the function has a minimum.

Recently, it was demonstrated \cite{44} that the local anisotropy plays an important role for the jamming effect in spherical bead systems. This research is in accordance with our ideas since we are not concerned with shapes of particles or local occupation probabilities, but rather consider polymer semiflexibility. However, it is not completely clear how the dynamic arrest is caused by the local anisotropy. To address this problem we mention the result in \cite{33}, where it was shown that the absence of lattice loops may amplify the effect of local anisotropy on averaged transport properties, which is shown for percolating resistors randomly distributed on the lattice. The breakage of the local anisotropy at the glass transition for the spherical beads can be explained in the framework of the theory of glass transition of Edwards and Vilgis \cite{45}, where the dynamic arrest is caused by closed path configurations. The loops get frozen first. This makes the transport of excitations preferentially along tree-like structures. Hence, the system creates more anisotropic local configurations due to their higher mobility in the tree environment.

The theory of Edwards and Vilgis shows how the dynamical properties of continuous models and equations can be transferred into discrete counterparts. Thus, we think that the configurational entropy, obtained by a proper discretization scheme, can be used to predict the rapid slowing down. Also, we suggest that the Nernst postulate formulated for the isotropic liquids should be supplemented by the idea of local anisotropy.
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9 Appendix

In this appendix we demonstrate that the entropy expression developed in the paper by Ryu and Gujrati [29] with added correction due to polymer semiflexibility is equivalent to [30]. Formulated for multicomponent mixtures their theory can easily be adopted to our system with minor corrections. One of these is due to discrepancy in methodology of accounting for the mer-mer interaction. In their theory this interaction is incorporated (as in the Flory-Huggins theory) through the effective interaction between occupied sites and vacancies with energy given by

$$\epsilon_{10} = \epsilon_{10} - 1/2(\epsilon_{11} + \epsilon_{00}),$$

where $\epsilon_{10}, \epsilon_{11}, \epsilon_{00}$ are the energies of physical interactions for mer-hole, mer-mer and hole-hole pairs, respectively. Since only the second is actually present, $\epsilon_{01} = 0, \epsilon_{11} = V, \epsilon_{00} = 0$, one gets $\epsilon_{10} = -V/2$, with $w = \exp(V/2RT)$ being the corresponding Boltzmann weight. Note also that $q$ in their symbolic representation is equivalent to $z$ in ours both signifying the coordination number. The semiflexibility can be incorporated by replacement of $r = q - 1$ in their paper by $r_f$ defined in [31] and by adding the term $-N_g \ln w_f$ to the entropy [see Eq. (57) below]. Here we summarize the results of their theory. The final equations resulting from the Bethe lattice iterative technique are the following:

$$y_{0,1} = \frac{(w + \lambda_1 y_{1}^{-1} y_{0,1}^{-1} / r_f) / (1 + w \lambda_1 y_{1}^{-1} y_{0,1}^{-1} / r_f),}{1/(1 - \theta) = 1 + (z/2)x y_{0,1} y_{1}^{-1} / r_f,}$$

$$Q_1 = 1 + w \lambda_1 y_{1}^{-1} y_{0,1}^{-1} / r_f,$$

where $\lambda_1 = (z/2)x - (x - 1)$ and the parameters $y_1, y_{0,1}, Q_1$ are evaluated from the relations

$$y_{0,1} = \left[-w(p - 1) + \sqrt{w^2(p - 1)^2 + 4p}\right] / 2,$$

$$Q_1 = 1 + wp / y_{0,1},$$

with $p = \theta \lambda_1 / (z/2)(1 - \theta)x$. Below we list the expressions for the the densities which are numbers of the corresponding species per lattice site:

$$\phi_{n,1} = \theta / x, \quad \phi_b = \phi_{n,1}(x - 1), \quad \phi_{00} = z(1 - \theta) / Q_1,$$

$$\phi_{01} = z(1 - \theta) - 2 \phi_{00}, \quad \phi_{11} = (z/2)(1 - \theta) - \phi_{01} - \phi_b,$$

$$\phi_{1u} = (z/2)(1 - \theta) - \phi_{0u} = (z/2)(1 - \theta), \quad \phi_u = z/2 - \phi_b,$$

where $\phi_{n,1}$ and $\phi_b$ are the densities of polymers and bonds, respectively; $\phi_{00}, \phi_{01}$ and $\phi_{11}$ are the densities of hole-hole, hole-mer and mer-mer nearest-neighbor contacts; $\phi_{0u}, \phi_{01}$ and $\phi_{11}$ are the corresponding athermal contact densities; $\phi_{1u}$ and $\phi_u$ are the densities of unoccupied lattice bonds with occupied sites and vacancies, respectively; $\phi_u$ is the density of unoccupied lattice bonds. The adimensional pressure, $\omega = \beta P v_0 (\beta = 1/k_B T)$, given by

$$\beta P v_0 = -\ln(1 - \theta) + (z/2) \ln(2\phi_u / z) + (z/2) \ln(\phi_{00} / \phi_{00}).$$

can be transformed to the form equivalent to (52):

$$\beta P v_0 = -\ln(1 - \theta) + (z/2) \ln[(1 - \theta) Q_1].$$

Finally, we compared the Ryu-Gujrati configurational entropy corrected to account for semiflexibility

$$S_n / k_B = (\phi_{n,1} \ln[(z/2)r_f^{-2} x / \phi_{n,1}] - (1 - \theta) \ln(1 - \theta) + \phi_{01} \ln(\phi_{01} / \phi_{01}) + \phi_{00} \ln(\phi_{00} / \phi_{00})$$

$$+ \phi_{11} \ln(\phi_{11} / \phi_{11}) - N_g \ln w_f / \theta)$$

with [33] and verified numerically their equivalency.

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