Statistical thermodynamics of polydisperse polymers

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A statistical thermodynamics theory of polydisperse polymers based on a lattice model of fluids is formulated. Pure polydisperse polymer can be completely characterized by three scale factors and the molecular weight distribution of the system. The equation of state does not satisfy a simple corresponding-states principle, except for a polymer fluid of sufficiently high molecular weight. The relationships between thermal expansion coefficient α and isothermal compressibility β with reduced variables are also predicted.

(Keywords: statistical thermodynamics; pure polymer; polydispersity; equation of state)

INTRODUCTION

The statistical thermodynamics of polymer solutions and blends is of increasing importance with the development of polymer science. However, for most theories of polymer solutions and blends, e.g. the Flory–Huggins[1] solution theory, the equation-of-state theory[2–9] and others[10–11], the polymer has been taken as a monodisperse fluid. When a polydisperse polymer system is considered, a correction factor[6] is introduced to reduce it to a monodisperse result. Polydispersity, which is an intrinsic attribute of polymers, is avoided. In the 1980s, Kleintjens and Koningsveld[12–16] used a mean-field lattice gas model for polymer fluids and considered multicomponent polymer systems, but the theory did not thoroughly solve the influences of polydispersity on phase separation.

In this paper, a polymer is regarded as a polydisperse fluid from the outset and is treated with the statistical thermodynamics of lattice fluids. Some important relationships can be obtained from the theory and the influence of polydispersity can be accounted for. The more generalized result reduces to the pure lattice fluid (LF) theory of Sanchez and Lacombe[7] as a special case when the polydispersity index, η, equals unity ($\eta = M_w/M_n$).

THEORY

Model description

Consider a polydisperse linear polymer system, consisting of a succession of molecules of different chain lengths and vacant lattice sites (holes). In this system, there are N_1 molecules each of which occupies r_1 sites (a r_1-mer), N_2 molecules each of which occupies r_2 sites (a r_2-mer), ..., N_k molecules each of which occupies r_k sites (a r_k-mer) and N_0 vacant lattice sites (holes), and the total number of molecules is N, where:

$$N = N_1 + N_2 + \ldots + N_k = \sum_{i=1}^{k} N_i \tag{1}$$

The total number of lattice sites for a system of N_1r_1-mers, N_2r_2-mers, ..., N_kr_k-mers and N_0 empty sites (holes) is:

$$\begin{aligned} N_r &= N_0 + r_1N_1 + r_2N_2 + \ldots + r_kN_k \\ &= N_0 + \sum_{i=1}^{k} r_iN_i \\ &= N_0 + rN \end{aligned} \tag{2}$$

where

$$r = \sum_{i=1}^{k} r_iN_i/N = \sum_{i=1}^{k} x_ir_i \tag{3}$$

$$x_i = N_i/N \tag{4}$$

The coordination number of the lattice is z. Each interior mer of a linear chain is surrounded by $(z-2)$ nearest non-bonded neighbours and two bonded neighbours; mers at the chain ends have $(z-1)$ nearest non-bonded neighbours and one bonded neighbour. Thus, each r_i-mer is surrounded by q_iz nearest non-bonded neighbours where:

$$\begin{aligned} q_iz &= (r_i-2)(z-2) + 2(z-1) \\ &= r_i(z-2) + 2 \end{aligned} \tag{5}$$

q_i will be regarded as a valid chain length to a r_i-mer.

The total number of nearest neighbour pairs in the system is $(z/2)N_r$. Only $(z/2)N_q$ are non-bonded pairs

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where:

$$N_q = N_0 + \sum_{i=1}^{k} q_i N_i \tag{6}$$

The numbers N_r, N_q, N_0 and N are correlated by:

$$(z/2)N_q = (z/2 - 1)N_r + N + N_0 \tag{7}$$

A r_i-mer is characterized by a symmetry number σ_i. For example, for a linear r_i-mer it is equal to two if the chain ends are indistinguishable and to unity if the chain ends are distinguishable.

A r_i-mer is also characterized by a 'flexibility parameter' δ_i. It is equal to the number of ways in which the r_i-mer can be arranged on the lattice after one of its mers has been fixed on a lattice site. It is a measure of the r_i-mer internal degrees of freedom. In general, for r_i-mer the maximum value for δ_i is:

$$(\delta_i)_{\max} = z(z-1)^{r_i - 2} \tag{8}$$

According to Guggenheim's derivation[17–19], the number of configurations available to a system consisting of $N_1 r_1$-mers, $N_2 r_2$-mers, …, $N_k r_k$-mers and N_0 empty sites is:

$$\begin{aligned}\Omega &= \left(\frac{\delta_1}{\sigma_1}\right)^{N_1}\left(\frac{\delta_2}{\sigma_2}\right)^{N_2}\cdots\left(\frac{\delta_k}{\sigma_k}\right)^{N_k}\frac{N_r!}{N_0!\,N_1!\,N_2!\ldots N_k!}\\ &\quad\times (N_q/N_r)^{z/2}\\ &= \left[\prod_{i=1}^{k}\left(\frac{\delta_i}{\sigma_i}\right)^{N_i}\right]\frac{N_r!}{\prod\limits_{i=0}^{k} N_i!}\left(\frac{N_q!}{N_r!}\right)^{z/2}\end{aligned} \tag{9}$$

As a result of the Flory approximation[20], when z is very large, we have:

$$\begin{aligned}\lim_{z\to\infty}\Omega &= \left(\frac{1}{f_0}\right)^{N_0}\left(\frac{\omega_1}{f_1}\right)^{N_1}\left(\frac{\omega_2}{f_2}\right)^{N_2}\cdots\left(\frac{\omega_k}{f_k}\right)^{N_k}\\ &= \left(\frac{1}{f_0}\right)^{N_0}\prod_{i=1}^{k}\left(\frac{\omega_i}{f_i}\right)^{N_i}\end{aligned} \tag{10}$$

$$\omega_i = \delta_i r_i/\sigma_i e^{r_i - 1} \tag{11}$$

and where the empty site fraction f_0 and the occupied sites fraction f_i are given by:

$$f_0 = N_0/N_r \tag{12}$$

$$f_i = r_i N_i/N_r \tag{13}$$

In this paper, all calculations will be based on equation (10) and it will be applied to all types of molecular geometries. In addition, the following assumptions will be made.

1. The flexibility parameter δ_i is independent of temperature and pressure.
2. The close-packed volume $r_i v^*$ of a molecule is independent of temperature and pressure.

The close-packed volume of a mer is v^*; it is also the volume of a lattice site. The close-packed volume of $N_1 r_1$-mers, $N_2 r_2$-mers, …, and $N_k r_k$-mers (no holes) is:

$$\begin{aligned}V^* &= (r_1 N_1 + r_2 N_2 + \ldots + r_k N_k)v^*\\ &= \sum_{i=1}^{k} r_i N_i v^* = rNv^*\end{aligned} \tag{14}$$

If ρ^* is the close-packed mass density, then the close-packed molecular volume is given by:

$$r_i v^* = M_i/\rho^* \tag{15}$$

where M_i is the molecular weight of r_i-mer. As a first approximation ρ^* is equal to the crystal density. Equation (15) provides a useful means of estimating the close-packed molecular volume, $r_i v^*$. The volume associated with an empty lattice site (a hole) is also equal to v^*; the volume of the system is therefore:

$$V = \left(N_0 + \sum_{i=1}^{k} r_i N_i\right)v^* = N_r v^* = V^*/f \tag{16}$$

where

$$f = \sum_{i=1}^{k} r_i N_i/N_r = \sum_{i=1}^{k} f_i \tag{17}$$

If the energy of the lattice depends only on nearest-neighbour interactions, the lattice energy (attractive) can be generally written as:

$$E = -(z/2)N_r \sum_i \sum_j p(i,j)\varepsilon_{ij} \tag{18}$$

where ε_{ij} is the pair interaction energy between components i and j and $p(i,j)$ is the pair (joint) probability of an (i,j) pair in the system. In the present case, there are only two components: hole and mer. The only non-zero pair-interaction energy is the one associated with non-bonded mer–mer interactions; hole–hole, hole–mer and bonded mer–mer pairs are assigned a zero energy. If random mixing of hole and molecules is assumed, i.e. the same approximation invoked in the evaluation of Ω, then the probability of a non-bonded, mer–mer interaction is[17–19]:

$$p(\text{mer, mer}) = \left(\sum_{i=1}^{k} q_i N_i\right)^2 \bigg/ N_q N_r \tag{19}$$

or in the large z limit becomes:

$$\lim_{z\to\infty} p(\text{mer, mer}) = \left(\sum_{i=1}^{k} r_i N_i/N_r\right)^2 = f^2 \tag{20}$$

Thus, from equations (18), (19) and (20), the lattice energy is:

$$E = -N_r(z\varepsilon/2)f^2 \tag{21}$$

By using equations (14) and (16), it follows:

$$E/rN = -\varepsilon^*(V^*/V) = -\varepsilon^* f \tag{22}$$

where ε is the non-bonded, mer–mer interaction energy and

$$\varepsilon^* = z\varepsilon/2 \tag{23}$$

is the total interaction energy per mer. The quantity $r_i\varepsilon^*$ is the characteristic interaction energy per molecule in the absence of holes; ε^* is also the energy required to create a lattice vacancy (hole).

Since E and Ω are functions of a single parameter, i.e. the number of holes in the lattice, the double sum over E and V required in the evaluation of the partition function can be replaced by a single sum over N_0:

$$Z(T,P) = \sum_{N_0=0}^{\infty} \Omega \exp[-\beta'(E + PV)] \tag{24}$$

where

$$\beta' = 1/kT \tag{25}$$

When the above sum is approximated to be its maximum term, the Gibbs free energy G is equal to:

$$G = E + PV - kT\ln\Omega \tag{26}$$

Using equations (10), (16), (21) and (26), G can be expressed in dimensionless variables as:

$$\begin{aligned}\tilde{G} &= G/rN\varepsilon^* \\ &= -\tilde{\rho} + \tilde{P}\tilde{v} + \tilde{T}\Bigg[(\tilde{v}-1)\ln(1-\tilde{\rho}) + \frac{1}{r}\ln\tilde{\rho} \\ &\qquad + \sum_{i=1}^{k}\left(\frac{\varphi_i}{r_i}\right)\ln\left(\frac{\varphi_i}{\omega_i}\right)\Bigg]\end{aligned} \tag{27}$$

$$\frac{1}{r} = 1\Big/\sum_{i=1}^{k} x_i r_i = \sum_{i=1}^{k}\left(\frac{\varphi_i}{r_i}\right) \tag{28}$$

where $\tilde{T}, \tilde{P}, \tilde{v}$ and $\tilde{\rho}$ are the reduced temperature, pressure, volume and density, respectively, i.e.

$$\tilde{T} = T/T^* \qquad T^* = \varepsilon^*/k \tag{29}$$

$$\tilde{P} = P/P^* \qquad P^* = \varepsilon^*/v^* \tag{30}$$

$$\tilde{v} = 1/\tilde{\rho} = V/V^* \qquad V^* = N(rv^*) \tag{31}$$

The total occupied sites fraction f and the empty site fraction f_0 are related to the mass density ρ and the close-packed mass density ρ^* by:

$$f = \rho/\rho^* = \tilde{\rho} = 1/\tilde{v} \tag{32}$$

$$f_0 = 1 - \tilde{\rho} \tag{33}$$

The minimum value of the free energy is found in the usual way:

$$\left.\frac{\partial\tilde{G}}{\partial\tilde{v}}\right|_{\tilde{T},\tilde{P}} = 0 \tag{34}$$

which yields:

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}\left[\ln(1-\tilde{\rho}) + \left(1-\frac{1}{r}\right)\tilde{\rho}\right] = 0 \tag{35}$$

$$PV/NkT = r\tilde{P}\tilde{v}/\tilde{T} = 1 - r[1 + \ln(1-\tilde{\rho})/\tilde{\rho} + \tilde{P}/\tilde{T}] \tag{36}$$

Equation (35) is the equation of state for the system. It must always be kept in mind that $\tilde{\rho}$ is a dependent variable and $\tilde{P}$ and $\tilde{T}$ are independent variables in the pressure ensemble. Equation (36) contains relations between the macroscopic variables and the reduced variables.

Equations (26), (27) and (35) contain the complete thermodynamic description of the model fluid; all other thermodynamic properties follow from standard thermodynamic formulae. For example, the thermal expansion coefficient α and isothermal compressibility β are given by:

$$\alpha \equiv \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_P = -\left.\frac{\partial\ln\tilde{\rho}}{\partial T}\right|_P \tag{37}$$

$$\beta \equiv -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_T = \left.\frac{\partial\ln\tilde{\rho}}{\partial P}\right|_T \tag{38}$$

$$T\alpha = \frac{1 + \tilde{P}\tilde{v}^2}{\tilde{T}\tilde{v}[1/(\tilde{v}-1) + 1/r] - 2} \tag{39}$$

$$P\beta = \frac{\tilde{P}\tilde{v}^2}{\tilde{T}\tilde{v}[1/(\tilde{v}-1) + 1/r] - 2} \tag{40}$$

Determination of molecular parameters

A pure fluid is completely characterized by three scale factors (T^*, P^* and ρ^*) and r (where r represents a mean value of chain-length distribution). The number of sites r_i occupied by the ith molecule and its molecular weight M_i are related to the scale factors by:

$$RT^*\rho^*/P^* = v^*\rho^* = M_i/r_i \tag{41}$$

and

$$P^*v^*/RT^* = 1 \tag{42}$$

where R is the gas constant.

Since r remains explicit in the reduced equation of state, a simple corresponding-states principle is not, in general, satisfied. However, for a polymer liquid

$$r = \sum_{i=1}^{k} x_i r_i \to \infty$$

and the equation of state reduces to:

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}[\ln(1-\tilde{\rho}) + \tilde{\rho}] = 0 \tag{43}$$

Thus, all polymer liquids of sufficiently high molecular weight should satisfy a corresponding-states principle. Equation-of-state parameters have been determined for the polymers by a non-linear least-squares fit of equation (43) to experimental density data[21–25].

For convenience, we assume that the scale factors have nothing to do with the molecular chain length. Thus, for a polydisperse polymer fluid, the scale factors are identical with the scale factors of sufficiently high molecular weight polymer liquids.

A special case

When the molecular weight of the system obeys a Flory distribution[26] in a system, i.e.

$$N_{r_i} = N^*(1-q)^2 q^{r_i-1} \tag{44}$$

then

$$r = \frac{1}{1-q} \tag{45}$$

$$q_i z = r_i(z-2) + 2 \tag{46}$$

$$N_r = N_0 + N^* \tag{47}$$

$$N_q = N_0 + \left(1 - \frac{2q}{z}\right)N^* \tag{48}$$

$$\Omega = \frac{N_r!}{N_0!}\left(\frac{N_q!}{N_r!}\right)^{z/2}\prod_{r_i}\left(\frac{\delta_{r_i}}{\sigma_{r_i}}\right)^{N^*(1-q)^2q^{r_i}-1} \tag{49}$$

$$\lim_{z\to\infty}\Omega = \left(\frac{1}{f_0}\right)^{N_0}\prod_{r_i}\left(\frac{\omega_{r_i}}{f_{r_i}}\right)^{N^*(1-q)^2q^{r_i}-1} \tag{50}$$

$$f_0 = N_0/N^*, \qquad f_{r_i} = r_i(1-q)^2q^{r_i-1} \tag{51}$$

where N^* is the total number of mers in the system; q, an independent variable, is the parameter of reaction extent; N_{r_i} is the number of r_i-mers; δ_{r_i} is the flexibility parameter of r_i-mer; σ_{r_i} is the symmetry number of

r_i-mer; and $\omega_{r_i} = \delta_{r_i} r_i / \sigma_{r_i} e^{r_i - 1}$. Thus, we have:

$$\tilde{G} = -\tilde{\rho} + \tilde{P}\tilde{v} + \tilde{T}\Big[(\tilde{v} - 1)\ln(1 - \tilde{\rho}) + (1 - q)\ln\tilde{\rho}(1 - q)^2 + q + q\ln q + (1 - q)^2 \sum_{r_i} q^{r_i - 1} \ln\frac{\sigma_{r_i}}{\delta_{r_i}} \Big] \qquad (52)$$

In a similar manner to the derivation of equations (35), (36), (39) and (40), we have:

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}[\ln(1 - \tilde{\rho}) + q\tilde{\rho}] = 0 \text{ (equation-of-state)} \qquad (53)$$

$$PV/N^*(1 - q)kT = \frac{1}{1 - q}\tilde{P}\tilde{v}/\tilde{T}$$

$$= 1 - \frac{1}{1 - q}[1 + \ln(1 - \tilde{\rho})/\tilde{\rho} + \tilde{P}/\tilde{T}] \qquad (54)$$

$$T\alpha = \frac{1 + \tilde{P}\tilde{v}^2}{\tilde{T}\tilde{v}[1/(\tilde{v} - 1) + (1 - q)] - 2} \qquad (55)$$

$$P\beta = \frac{\tilde{P}\tilde{v}^2}{\tilde{T}\tilde{v}[1/(\tilde{v} - 1) + (1 - q)] - 2} \qquad (56)$$

These results are identical with equations (35), (36), (39) and (40) if $1/1 - q$ is substituted by r.

DISCUSSION AND CONCLUSIONS

From the above derivation it is shown that the effect of polydispersity on the equation of state cannot be ignored, except for polymer liquids of sufficiently high molecular weight. The equation-of-state, $T\alpha$, and $P\beta$ are affected by $1/r$ when the molecular weight of polymer liquid is not very high or the distribution of molecular weights is not very narrow. The influence of polydispersity or r decreases with increase of molecular weight or r and increases with distribution width. When $\eta = 1$, i.e. the polymer fluid is monodisperse, our theory reduces to the lattice-fluid theory of Sanchez and Lacombe[7] for a monodisperse system. In this case, $r_i = r$, $\delta_i = \delta$, $\sigma_i = \sigma$, $\omega_i = \omega$, $\varphi_i = 1$ and the summation over i is not needed, thus we have:

$$\tilde{G} = -\tilde{\rho} + \tilde{P}\tilde{v} + \tilde{T}\left[(\tilde{v} - 1)\ln(1 - \tilde{\rho}) + \frac{1}{r}\ln\left(\frac{\tilde{\rho}}{\omega}\right) \right] \qquad (57)$$

and

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}\left[\ln(1 - \tilde{\rho}) + \left(1 - \frac{1}{r}\right)\tilde{\rho} \right] = 0 \qquad (58)$$

where r (a constant) is the number of sites which an r-mer occupies. This is identical to the LF theory for a monodisperse system[7]. The forms of the expressions for $T\alpha$ and $P\beta$ are the same as those in equations (39) and (40), except that r is distinct.

When $q = 0$, the polydispersity index (η) is equal to unity for a Flory distribution. Then, we can obtain:

$$\tilde{G} = \tilde{\rho} + \tilde{P}\tilde{v} + \tilde{T}\left[(\tilde{v} - 1)\ln(1 - \tilde{\rho}) + \ln\tilde{\rho} + \ln\left(\frac{\sigma}{\delta}\right) \right] \qquad (59)$$

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}\ln(1 - \tilde{\rho}) = 0 \qquad (60)$$

$$T\alpha = \frac{1 + \tilde{P}\tilde{v}^2}{\dfrac{\tilde{T}\tilde{v}^2}{\tilde{v} - 1} - 2} \qquad (61)$$

$$T\beta = \frac{\tilde{P}\tilde{v}^2}{\dfrac{T\tilde{v}^2}{\tilde{v} - 1} - 2} \qquad (62)$$

This is the same as the LF theory for a monodisperse system when $r = 1$.

The main conclusions of this paper are summarized as follows.

1. Only three scale factors and the molecular-weight distribution are required to describe a polydisperse polymer fluid. These scale factors can be determined for a polymer of sufficiently high molecular weight.
2. Polymer liquids of sufficiently high molecular weight satisfy a corresponding-states principle.
3. The influence of polydispersity decreases with increase of molecular weight and increases with distribution width.
4. The LF theory of Sanchez and Lacombe[7] for monodisperse polymers is a special case of the present theory.
5. The present theory is a special case of the LF theory of Lacombe and Sanchez[8] for fluid mixtures which are regarded as the same fluid.

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