Statistical thermodynamics of a lattice fluid: pure polymer

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A statistical thermodynamics theory of a polydisperse polymer based on a lattice model of a fluid is formulated. The pure polydisperse polymer is completely characterized by three scale factors and the distribution law of the system. The equation of state does not satisfy a simple corresponding state principle, except for the polymer fluid with sufficiently high molecular weight.

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

Introduction

For all the theories of polymer solutions up to now, e.g. Flory–Huggins[1] solution theory, the equation-of-state theory[2–9] and other theories[10,11], the polymer has always been taken as a monodisperse fluid. When a polydisperse polymer system is considered, a correction factor[6] is introduced to reduce it into the monodisperse result. In this paper, a polymer is regarded as a polydisperse fluid from the outset and the polymer fluid is dealt with by the approach of statistical thermodynamics on the basis of a lattice fluid.

Model description and results

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

$$N = \sum_{i=1}^{k} N_i \tag{1}$$

The total number of lattice sites for a system of N_1 r_1-mers, N_2 r_2-mers, ..., N_k r_k-mers and N_0 empty sites (holes) is

$$N_r = N_0 + \sum_{i=1}^{k} r_i N_i = N_0 + rN \tag{2}$$

where

$$r = \sum_{i=1}^{k} r_i N_i / N = \sum_{i=1}^{k} x_i r_i \tag{3}$$

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

The coordination number of the lattice is z. For a linear polymer, each r_i-mer is surrounded by $q_i z$ nearest non-bonded neighbours where

$$q_i z = r_i(z-2) + 2 \tag{5}$$

where q_i is the effective chain length, where each mer is surrounded by z nearest non-bonded neighbours in a q_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 where

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

A r_i-mer is characterized[7] by a symmetry number σ_i and is also characterized[7] by a 'flexibility parameter' δ_i.

According to Guggenheim's derivation[12–14], the number of configurations available to the system is

$$\Omega = \left(\frac{\delta_1}{\sigma_1}\right)^{N_1} \left(\frac{\delta_2}{\sigma_2}\right)^{N_2} \cdots \left(\frac{\delta_k}{\sigma_k}\right)^{N_k} \frac{N_r!}{\prod_{i=0}^{k} N_i!} \left(\frac{N_q!}{N_r!}\right)^{z/2} \tag{7}$$

As a result of the 'Flory approximation'[15], we have

$$\lim_{z\to\infty} \Omega = \left(\frac{1}{f_0}\right)^{N_0} \prod_{i=1}^{k} \left(\frac{\omega_i}{f_i}\right)^{N_i} \tag{8}$$

where

$$\omega_i = \delta_i r_i / \sigma_i \, e^{r_i - 1} \tag{9}$$

$$f_0 = N_0/N_r \tag{10}$$

$$f_i = r_i N_i / N_r \tag{11}$$

where f_0 and f_i are the empty and occupied site fractions, respectively.

In this paper, all calculations will be based on equation (8). In addition, the following assumptions will be made: the flexibility parameter δ_i is independent of temperature and pressure; 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^*. Then, the total close-packed volume of the system is

$$V^* = \sum_{i=1}^{k} r_i N_i v^* = rNv^* \tag{12}$$

If the volume associated with an empty lattice site (a

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hole) is also equal to v^*, the volume of the system is

$$V = N_r v^* = V^*/f \tag{13}$$

where

$$f = \sum_{i=1}^{k} r_i N_i / N_r = \sum_{i=1}^{k} f_i \tag{14}$$

The lattice energy (attractive) that depends only on nearest neighbour interactions is

$$E = -(z/2) N_r \sum_i \sum_j p(i,j)\varepsilon_{ij} \tag{15}$$

where ε_{ij} is the pair interaction energy between components i and j, and

$$\varepsilon_{ij} \begin{cases} \neq 0 & \text{(non-bonded mer–mer interactions)} \\ = 0 & \text{(other interactions)} \end{cases} \tag{16}$$

If we assume random mixing of holes and molecules, then the probability of a non-bonded mer–mer interaction[12–14] is

$$p(\text{mer, mer}) = \left(\sum_{i=1}^{k} q_i N_i\right)^2 \Big/ N_q N_r \tag{17}$$

or in the large z limit becomes

$$\lim_{z\to\infty} p(\text{mer, mer}) = \left(\sum_{i=1}^{k} r_i N_i / N_r\right)^2 = f^2 \tag{18}$$

Thus, the lattice energy is

$$E = -N_r (z\varepsilon/2) f^2 = -rN\varepsilon^* f = -rN\varepsilon^*(V^*/V) \tag{19}$$

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

$$\varepsilon^* = z\varepsilon/2 \tag{20}$$

is the total interaction energy per mer.

The partition function of this system is

$$Z(T,P) = \sum_{N_0=0}^{\infty} \Omega \exp[-\beta(E + PV)] \tag{21}$$

and the Gibbs free energy is equal to

$$G = -kT \ln Z(T,P) \doteq E + PV - kT \ln \Omega \tag{22}$$

Using equations (8), (13) and (19), G can be expressed as a dimensionless variable:

$$\begin{aligned} \tilde{G} &= G/rN\varepsilon^* \\ &= -\tilde{\rho} + \tilde{P}\tilde{v} + \tilde{T}\left[(\tilde{v} - 1)\ln(1 - \tilde{\rho}) + \frac{1}{r}\ln\tilde{\rho} \right. \\ &\quad \left. + \sum_{i=1}^{k}\left(\frac{\varphi_i}{r_i}\right)\ln\left(\frac{\varphi_i}{\omega_i}\right)\right] \end{aligned} \tag{23}$$

where

$$\varphi_i = r_i N_i / rN \tag{24}$$

$$\tilde{T} = T/T^* \qquad T^* = \varepsilon^*/k \tag{25}$$

$$\tilde{P} = P/P^* \qquad P^* = \varepsilon^*/v^* \tag{26}$$

$$\tilde{v} = 1/\tilde{\rho} = V/V^* \tag{27}$$

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

$$\left.\frac{\partial \tilde{G}}{\partial \tilde{v}}\right|_{\tilde{T},\tilde{P}} = 0 \tag{28}$$

which yields

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}\left[\ln(1 - \tilde{\rho}) + \left(1 - \frac{1}{r}\right)\tilde{\rho}\right] = 0 \tag{29}$$

when $r \to \infty$, the equation of state becomes

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}[\ln(1 - \tilde{\rho}) + \tilde{\rho}] = 0 \tag{30}$$

Thus, the polymer fluid of sufficiently high molecular weight satisfies a simple corresponding state principle.

If the polymer fluid is monodisperse, i.e. $r_i = r$, $\delta_i = \delta$, $\sigma_i = \sigma$, $\varphi_i = 1$, and the summation of i is deprived, then we have

$$\tilde{G} = -\tilde{\rho} + \tilde{P}\tilde{v} + \tilde{T}\left[(\tilde{v} - 1)\ln(1 - \tilde{\rho}) + \frac{1}{r}\ln(\tilde{\rho}/\omega)\right] \tag{31}$$

and

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}\left[\ln(1 - \tilde{\rho}) + \left(1 - \frac{1}{r}\right)\tilde{\rho}\right] = 0 \tag{32}$$

where r is a constant and the number of sites which a r-mer occupies and $\omega = r\delta/\sigma\, e^{r-1}$. Thus, this theory can be reduced to the pure lattice fluid theory of Sanchez and Lacombe[7] when the polymer fluid is monodisperse.

From the above discussion, it can be shown that our theory is a general theory and the pure lattice fluid theory of Sanchez and Lacombe is only a special case of our theory.

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