Virial Series for a Lattice Gas Model of Polymerization

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ABSTRACT: A two-dimensional lattice gas model of associating monomers that can bond to at most two other monomers, thus forming flexible polymer chains, is treated. The exact first nine coefficients in the activity series (or, alternatively, the virial coefficients) for the pressure are derived as a function of a parameter measuring the bonding strength. From this series expressions are constructed for the average degree of polymerization as a function of density and temperature. The low-density series are very erratic and do not yield to the usual techniques for analysis of series expansions (ratios, Padé approximants). The effect of excluded volume in the model forces the system to exist in a zigzag structure with infinite degree of polymerization in the high-density limit. Limited series expansions are given for the breakdown of the high-density order. The high-density series are very well-behaved, and we are able to obtain a rough estimate of the critical density for the disappearance of long-range order in the system.

1. Introduction

Lattice models have played an important role in understanding the properties of macromolecules in solution.[1,2] A recent review is available.[3] In this paper we give exact virial series for a lattice gas model where the monomer units can associate to form flexible polymers. The model exactly treats the effect of excluded volume, making a polymer unit unapproachable once it has saturated its bivalent binding capability. Because of the excluded-volume effect in the model, the system undergoes an order–disorder transition at high density. While lattice gas models are primitive models for real systems, they do allow one to investigate phenomena, such as the existence of singularities associated with phase transitions, in greater detail than is the case for more realistic models. In particular for the lattice gas model one is able to calculate exactly a large number of terms in various low- and high-density series expansions.

The model that we will treat is illustrated in Figure 1. We consider monomer units on the plane square lattice where a particle can bond to at most two other particles, thus producing flexible polymer chains. Units at the end of a chain never lose their ability to react further, thus lengthening the chain (i.e. the model is analogous to a living polymer). In Figure 1 the monomer units are represented by solid dots, with bonds represented by solid lines. Each bond will contribute a Boltzmann factor, x, to the partition function

$$x = \exp(-\epsilon/kT) \tag{1.1}$$

where ϵ is the attractive (negative) interaction or bonding energy. Once a particle has saturated its valence by bonding to two other particles, a third particle is not allowed to sit at a nearest-neighbor lattice site. Such excluded sites are illustrated with open circles in Figure 1. The sites marked with crosses indicate loci where a particle could bond to the existing polymer. Some more extended structures are illustrated in Figure 2 where, again, the excluded sites are indicated with open circles. Note that closed polygons are allowed.

An interesting feature of the model is that, because of the excluded-volume effect, there are two high-density structures representing an infinite degree of polymerization. These are shown in Figure 3. The zigzag structure shown in Figure 3a has a density of 2/3 while the linear structure shown in Figure 3b has a density of 1/2. The structure of Figure 3a will be forced on the system as the density approaches 2/3. In Figure 3a there is a repeating pattern of two diagonals occupied by particles and one empty diagonal (because of the excluded-volume effect). This regular structure defines a particular sublattice structure that is not present at low density. The critical density at which this structure begins to lock in represents a second-order transition in this system.

In this paper we will use low- and high-density series expansions to study this model polymerization system. In the next section we turn to the low-density series.

2. Low-Density Series

We will formally treat our model as a single component system (the polymerizing monomers). One can think of the empty lattice sites as being occupied by neutral solvent molecules.

The pressure for our lattice gas model is given in the usual manner as a Mayer series in the activity z (where kT has the usual meaning):

$$p/kT = \sum_{n=1}^{\infty} b_n(x) z^n \tag{2.1}$$

We have used the Toeplitz matrix technique of Springgate and Poland[4] to obtain the $b_n(x)$ for this model exact through $n = 9$. These coefficients as a function of the bonding parameter x, given in (1.1), are listed in the Appendix.

For the special case of $x = 1$ we have determined the series through $n = 11$. This series is given below.

$$p/kT = z - (1/2)z^2 + (1/3)z^3 - 4(1/2)z^4 + 19(1/5)z^5 - 29(1/6)z^6 - 72(6/7)z^7 + 462(7/8)z^8 - 1141(8/9)z^9 + 4031(2/5)z^{10} - 29836(10/11)z^{11} + \ldots \tag{2.2}$$

The density is obtained in the usual fashion

$$\rho = \frac{\partial(p/kT)}{\partial \ln z} \tag{2.3}$$

For $x = 1$, the series in (2.2) gives

$$\rho = z - z^2 + z^3 - 17z^4 + 96z^5 - 175z^6 - 510z^7 + 3703z^8 - 10277z^9 + 40314z^{10} - 328206z^{11} + \ldots \tag{2.4}$$

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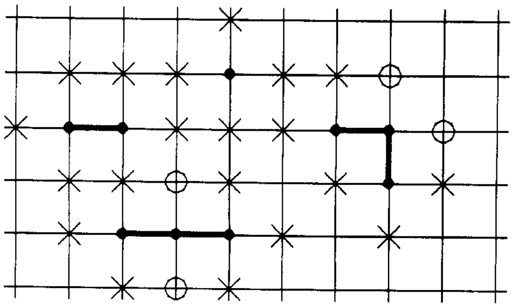

Figure 1. Lattice gas model of polymerization. Monomer units (solid dots) can have up to two nearest neighbors, but no more (the open circles represent sites that are forbidden for occupancy; the crosses indicate nearest-neighbor bonding sites).

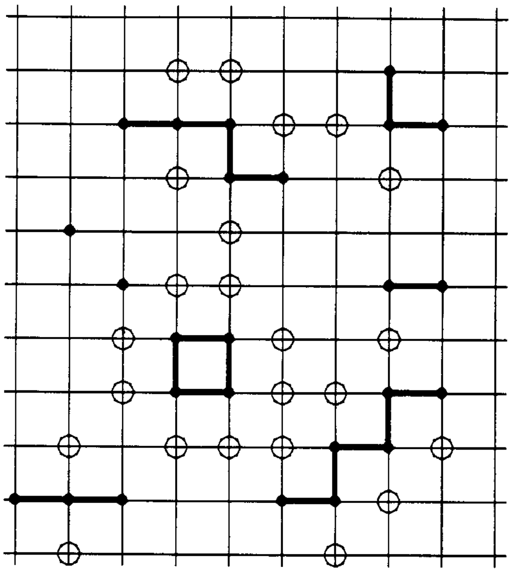

Figure 2. The lattice gas model of Figure 1 showing higher degrees of association (flexible chains). The open circles are nearest-neighbor sites forbidden by the excluded-volume effect (a monomer cannot sit next to a doubly bonded unit).

which can be inverted to give z as a function of ρ

$$z = \rho + \rho^2 + \rho^3 + 17\rho^4 + 2\rho^5 - 154\rho^6 + 1164\rho^7 - 964\rho^8 - 22639\rho^9 + 141857\rho^{10} - 86627\rho^{11} + \ldots \quad (2.5)$$

Inserting (2.5) in (2.2) gives the virial expansion for the pressure at $x = 1$:

$$p/kT = \rho + (1/2)\rho^2 + (1/3)\rho^3 + 12\rho^4 - 12(4/5)\rho^5 - 132(1/3)\rho^6 + 999(1/7)\rho^7 - 1709(5/8)\rho^8 - 17105(8/9)\rho^9 + 126921(1/10)\rho^{10} - 176029(10/11)\rho^{11} + \ldots \quad (2.6)$$

As a model for a system of associating monomers, it is of interest to calculate the average degree of polymerization. This is easily accomplished by noting that the b_n of the Appendix are finite polynomials in x, the bonding parameter:

$$b_n = \sum_{m=0}^{n} \alpha_m(n)x^m \quad (2.7)$$

Given n particles, the more bonds, the fewer independent polymer molecules there are. For $m = 0$ there are n-independent monomers, while for $m = (n - 1)$ there is a single polymer consisting of n units with $(n - 1)$ bonds. There are special cases corresponding to rings which could be treated specially. Some of the rings that contribute are shown in Figure 4. The single square (x^4) would contribute to b_4, while the large square (x^8) and the two smaller squares ($x^4 + x^4$) would contribute to b_8. The square with six sides is forbidden because of the excluded-volume effect (doubly bonded units cannot occupy nearest-neighbor sites; in the square the doubly bonded particles are located diagonally with respect to one another—on next nearest-neighbor lattice sites). In the present discussion we will ignore the special effect of loops and consider this as a minor correction. In this approximation we introduce a counting parameter, y, that counts the number of polymers as

$$b_n = \sum_{m=0}^{n-1} \alpha_m(n)x^m y^{n-m} \quad (2.8)$$

The probability that a lattice site contains the end of a polymer chain is then

$$\rho_e = \left(\frac{\partial(p/kT)}{\partial y}\right)_{y=1} \quad (2.9)$$

where we set $y = 1$ so as not to influence the thermodynamics of the system (y is simply a counting variable).

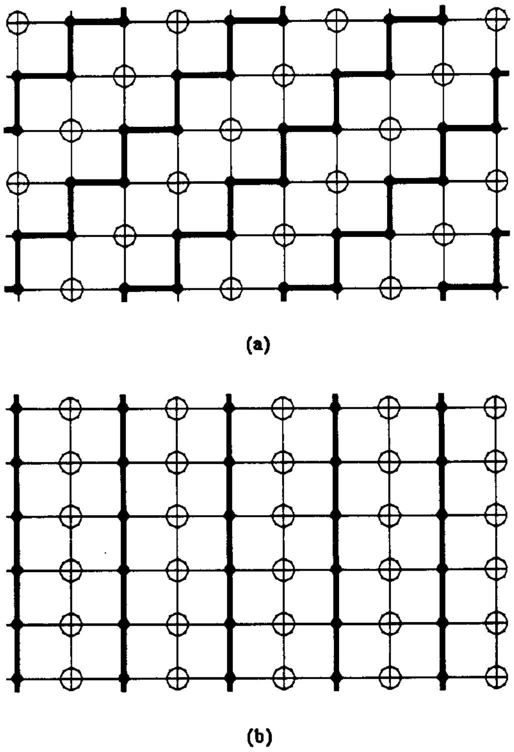

Figure 3. Illustration of two regular high-density structures. (a) The zigzag structure with density of 2/3. (b) The linear structure with density of 1/2.

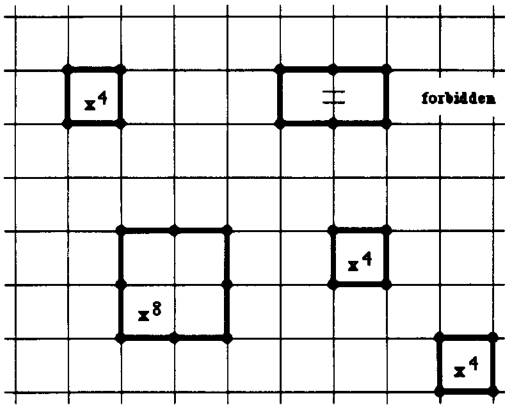

Figure 4. Illustration of allowed and forbidden cyclic configurations.

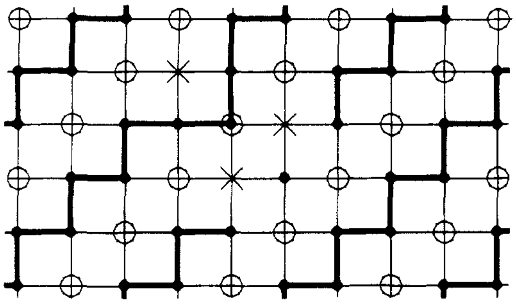

Figure 5. Introduction of defects into the high-density zigzag structure. The crosses indicate particles removed from the perfect zigzag structure; one such particle has been moved onto an originally vacant sublattice site.

Using (2.9) and (2.8), we have

$$\rho_e = \sum_{n=1}^{\infty}\left(\sum_{m=0}^{n-1} (n - m)\alpha_m(n)x^m\right)z^n \tag{2.10}$$

The averate degree of polymerization is then simply

$$\langle L \rangle = \frac{\rho}{\rho_e} = \frac{\sum_{n=1}^{\infty} n\left(\sum_{m=0}^{n-1} \alpha_m(n)x^m\right)z^n}{\sum_{n=1}^{\infty}\left(\sum_{m=0}^{n-1} (n - m)\alpha_m(n)x^m\right)z^n} \tag{2.11}$$

Using the coefficients given in the Appendix, one has the following explicit expressions for $\langle L \rangle$ evaluated at $x = 1$

$$\langle L \rangle = (1 - z + z^2 - 17z^3 + 96z^4 - 175z^5 - 510z^6 + 3703z^7 - 10277z^8 + ...)/(1 - 3z + 5z^2 - 11z^3 + 84z^4 - 447z^5 + 1206z^6 - 825z^7 - 3909z^8 + ...) \tag{2.12}$$

and at $x = 5$ (because of the size of the numbers we show only through the z^5 terms)

$$\langle L \rangle = \frac{1 + 15z + 241z^2 + 3151z^3 - 55824z^4 - 640239z^5 + ...}{1 + 5z + 21z^2 - 939z^3 - 20764z^4 - 42639z^5 + ...} \tag{2.13}$$

One could use the analogue of (2.5) for general x to give $\langle L \rangle$ as an explicit function of x. Expanding out the ratios, one then obtains the first eight terms in the exact expansion of $\langle L \rangle$ as a function of ρ. For $x = 1$ one has

$$\langle L \rangle = 1 + 2\rho + 4\rho^2 - 4\rho^3 + 4\rho^4 + 150\rho^5 - 676\rho^6 + 144\rho^7 + 15588\rho^8 + ... \tag{2.14}$$

while at $x = 5$

$$\langle L \rangle = 1 + 10\rho + 20\rho^2 + 20\rho^3 - 90940\rho_4 + 5.644 \times 10^6\rho^5 - 2.075 \times 10^8\rho^6 + 5.573 \times 10^9\rho^7 - 1.445 \times 10^{11}\rho^8 + ... \tag{2.15}$$

3. High-Density Series

As we pointed out in the Introduction, in the limit of high density the system takes on the zigzag structure shown in Figure 3a, where the maximum density is 2/3. Starting with the perfect zigzag structure one can systematically remove particles, introducing holes and rearrangements into the perfect high-density structure. This process is illustrated in Figure 5 where the crosses mark where three particles have been removed from the original zigzag structure; one of the particles has been moved onto a sublattice site (which we define as a site that was originally vacant in the high density structure). Our analysis will follow that of other lattice gas models.[5-7]

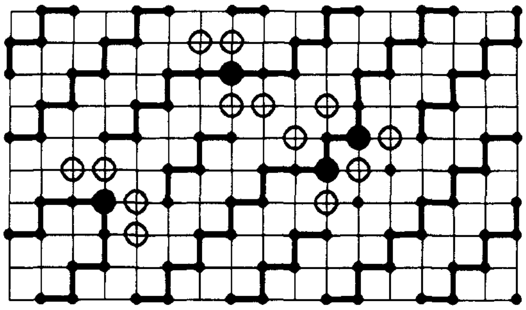

Figure 6. Illustration of extensive introduction of defects into the high-density zigzag structure. The open circles represent particles removed from the original zigzag structure (labeled with the ξ parameter) while the large solid circles represent particles moved onto the originally vacant sublattice (labeled with the ζ parameter).

Taking as an index the number of particles removed from the perfect high-density structure, we can construct the high-density grand partition function. We note that every particle in the high-density structure contributes a factor (zx) to the grand partition function (every particle contributes a factor z; each particle has two bonds to its nearest neighbors, but each bond is shared by two particles; hence each contributes a single x factor). We take M as the number of particles in the high-density limit

$$M = 2N/3 \tag{3.1}$$

where N is the number of lattice sites. The grand partition function can then be written as

$$\Xi = e^{pN/kT} = (zx)^M[1 + Mw + ...] \tag{3.2}$$

where w is the activity of a hole

$$w = \frac{1}{zx^2} \tag{3.3}$$

since for each isolated particle removed one loses a factor z and two factors x. In (3.2) the term "1" in the bracket represents the perfect high-density limit, while the Mw term gives the number of ways of removing one particle etc.

It is useful to introduce two additional activity-like factors. These are

ξ (counts the number of particles removed from the original zigzag structure)

ζ (counts the number of particles placed on the originally empty sublattice) (3.4)

The assignment of these factors is illustrated in Figure 6. The open circles represent particles removed from the original zigzag configuration; each such particle is assigned a factor ξ. The large dark circles represent particles moved onto the sublattice (originally vacant); each such particle is assigned a factor ζ.

The pressure is obtained in the usual manner

$$p/kT = \frac{1}{N} \ln \Xi = \frac{2}{3}[\ln (zx) + \sum_{n=1}^{\infty} b_n' w^n] \tag{3.5}$$

where the b_n' are the coefficients in the high-density activity series.

As seen from Figure 6, as one begins to remove particles, a large number of lattice rearrangements are possible. We have determined the b_n' as a function of x (the bonding parameter) and ζ and ξ (the two sublattice activities or counting parameters) through $n = 3$ by direct enumeration:

$$b_1 = \xi$$
$$b_2' = [-1(1/2) + x]\xi^2 + \zeta\xi^2$$
$$b_3' = [3(1/3) - 4x + x^2]\xi^3 + [(1/2)x^{-2} - 5 + 4x + 3x^2]\zeta\xi^4 + 3\zeta^2\xi^5 + \zeta^3\xi^6 \quad (3.6)$$

Using the coefficients in (3.6), we can calculate two densities:

ρ' = density of particles on the two originally fully occupied zigzag

ρ'' = density of particles on the original vacant sublattice (3.7)

These densities are given by the following relations:

$$\rho' = \frac{2}{3} - \left(\frac{\partial(p/kT)}{\partial\xi}\right)_{\xi=1}$$
$$\rho'' = \left(\frac{\partial(p/kT)}{\partial\zeta}\right)_{\zeta=1} \quad (3.8)$$

We set ξ and ζ equal to one so that they do not influence the thermodynamics (they serve solely as markers to count the appropriate sites).

As the density in increased from the low-density side, there will at first be no tendency for particles to segregate themselves in any kind of sublattice structure (as shown in Figure 3a). Thus at low density

$$\rho' = 2\rho/3$$
$$\rho'' = \rho/3 \quad (3.9)$$

or

$$\rho'/2 - \rho'' = 0 \quad (3.10)$$

At the other extreme, in the limit of close packing

$$\rho' = 2/3$$
$$\rho'' = 0 \quad (3.11)$$

Using (3.10) and (3.11) as guides, we define the following order parameter

$$R = 3\left(\frac{1}{2}\rho' - \rho''\right) = \begin{cases} 1 \text{ at close packing} \\ 0 \text{ at low density} \end{cases} \quad (3.12)$$

The parameter R will be exactly zero at low density for a finite range of densities. The density at which the sublattice structure begins to lock in is the critical density for this system. A similar order–disorder transition occurs in a hard particle lattice gas with nearest-neighbor exclusion.[5] In that model the particles form an ordered structure at high density with every other lattice site being occupied; since there is no requirement for such a regular structure at low densities, there is an analogous breakdown of order as the density is decreased. In that and similar[7] 2-D lattice gas models the transition is second order (as determined by the analysis of very long series expansions and in one case an exact solution[8]), R going continuously to zero with no jump discontinuity as found in a first-order transition. In systems with a first-order phase transition it is usually possible (for example, in the standard 2-D and 3-D Ising models) to obtain a low-temperature expansion for the coexistence curve.[9] For the 1-D Ising model such a low-temperature expansion does not exist[10] (since the second-order critical point is at absolute zero); the nonexistence of a low-temperature expansion for the coexistence curve is good evidence that the transition is second-order rather than first-order. The present model does not have a low-temperature expansion for the coexistence curve (since the bonding in the polymers is similar to that in clusters in the 1-D Ising model). For the reasons just cited we postulate that the transition is second order and hence seek the transition density at which $R(\rho_0) = 0$.

With (3.6) we can construct both w and ρ_0 series for R, where ρ_0 is the density of holes

$$\rho_0 = \frac{2}{3} - \rho$$
$$\rho = \frac{\partial(p/kT)}{\partial \ln z} = \frac{2}{3}[1 - \sum_{n=1}^{\infty} nb_n'w^n] \quad (3.13)$$

It is convenient to introduce a scaled density variable

$$\rho^* = \frac{3}{2}\rho_0 \qquad \rho = \frac{2}{3}(1 - \rho^*) \quad (3.14)$$

One obtains

$$R = 1 - w - (2 + 2x)w^2 - (3x^{-2} + 19 + 12x + 21x^2)w^3 + \dots \quad (3.15)$$

$$R = 1 - \rho^* - 3\rho^{*2} - [1(1/2)x^{-2} + 18 + 9x^2]\rho^{*3} + \dots \quad (3.16)$$

At $x = 1$ these become simply

$$R = 1 - w - 4w^2 - 55w^3 + \dots$$
$$R = 1 - \rho^* - 3\rho^{*2} - 28(1/2)\rho^{*3} + \dots$$

The series in (3.15) and (3.16) allow us to make a rough estimate of the critical values of the appropriate expansion variables. We will concentrate on calculating ρ_σ, the critical value of the density at which $R \rightarrow 0$ from the high-density side. First we can calculate successively estimates of ρ_σ by truncating (3.16) at the linear term, at the quadratic term, and then at the cubic term and calculating the value of ρ^* that makes the function zero. At $x = 1$ these equations give (using (3.14) to translate to ρ): $\rho_\sigma = 0$ (linear), $\rho_\sigma = 0.377$ (quadratic), and $\rho_\sigma = 0.490$ (cubic). Only the coefficient of the cubic term depends on x; one finds for the truncation at the cubic term: $\rho_\sigma = 0.503$ ($x = 1.5$), $\rho_\sigma = 0.516$ ($x = 2.0$). Thus increasing x (lowering the temperature) has the effect of moving the critical density slightly to higher values. The three estimates at $x = 1$ (0.000, 0.377, and 0.490) seem to be moving rapidly, though smoothly, to a high value of ρ_σ (recall that the maximum possible density is 2/3).

The study of other simple hard-core lattice gases where there is a similar order–disorder transition (locking in of sublattice order at a critical density) indicates the following behavior of the order parameter[5,6]

$$R \sim (1 - \rho^*/\rho_\sigma)^{1/8} \quad (3.17)$$

that is, $R \rightarrow 0$ with the famous Onsager exponent for the coexistence curve of the 2-D Ising model. If this form also holds for this model, then we expect

$$\left(\frac{1}{R}\right)^8 \sim \frac{1}{1 - \rho^*/\rho_\sigma} \quad (3.18)$$

i.e. this function should have a simple pole at $\rho^* = \rho_\sigma$. In addition, the ratio of successive coefficients should equal $1/\rho_\sigma$. At $x = 1$ one finds

$$(1/R)^8 = 1 + 8\rho^* + 60\rho^{*2} + 564\rho^{*3} + \dots \quad (3.19)$$

From the ratios of successive coefficients, converting to ρ using (3.14), one obtains the series of estimates of ρ_σ: 0.58, 0.58, 0.60. These numbers together with the values obtained from the truncated forms for R indicate that the critical density is probably close to 0.6.

That we are able to obtain such an estimate from a three-term series points up the general fact that high-density series for lattice gas models are very well-behaved. Clearly it would be nice to have longer series. The problem is (and it is also the most interesting feature of the model) that once one starts removing even a few particles from the high-density structure, the number of possible rearrangements of the remaining particles is very large. Thus the problem is not just counting the number of ways to place n holes (the analogue of the process used to construct the low-density series).

4. Discussion

Lattice gas models and lattice models of polymer solutions have proved to be useful caricatures of how real systems behave. In the present case we have been able to derive the exact first nine virial coefficients for a model polymerization system with the property that the bonding capacity of a monomer unit saturates at two (bivalent) and that once the valence of a unit is saturated, another unit cannot occupy a nearest-neighbor site. Thus the model represents a flexible growing chain with excluded volume. The excluded-volume effect forces the system to take up the zigzag configuration at high density, forcing the system to have a order–disorder transition.

We have seen that the high-density series work very well, even for the limited three-term series that we have derived. The low-density series on the other hand are very erratic. In general low-density expansions work well as density series in the high-temperature limit ($x = 1$). Usually one can pick up the order–disorder transition as a singularity in the appropriate low-density function.[5–7] One of the most useful functions in this regard is the modified compressibility ($K_T = \chi/(kT\rho^2)$ where K_T is the ordinary isothermal compressibility and χ is the analogue of the susceptibility in the magnet)

$$\chi = \frac{\partial \rho}{\partial \ln z} = \sum_{n=1}^{\infty} n^2 b_n z^n \qquad (4.1)$$

which can (using (2.5)) then be converted to a density series. At $x = 1$ one finds (there is no ρ^3 term)

$$\chi(\rho) = \rho - \rho^2 - 48\rho^4 + 156\rho^5 + 612\rho^6 - 6336\rho^7 + 15604\rho^8 + 73672\rho^9 - 714644\rho^{10} + 1419624\rho^{11} + \ldots \qquad (4.2)$$

One expects $\chi(\rho)$ to be singular at ρ_σ as

$$\chi \sim \left(\frac{1}{1 - \rho/\rho_\sigma}\right)^\gamma \qquad (4.3)$$

None of the usual techniques for analyzing series[5–11] (ratios, Padé approximants, etc.) seem to find any consistent pattern of estimates of ρ_σ.

While $\chi \to \infty$ at ρ_σ, χ^{-1} will go to zero at the same point. Forming $\chi^{-1}(\rho)$ one has

$$\rho\chi^{-1} = 1 + \rho + \rho^2 + 49\rho^3 - 59\rho^4 - 779\rho^5 + 7141\rho^6 - 13215\rho^7 - 154331\rho^8 + 1281901\rho^9 - 1906739\rho^{10} + \ldots \qquad (4.4)$$

One can try to estimate ρ_σ by calculating the value of ρ that makes $\chi^{-1} = 0$ for various stages of truncation of the series in (5.4). Again, no sensible pattern emerges. Thus while the existence of the order–disorder transition is transparent from the high-density series, the low-density series do not yield any hint of a transition occurring at high density. The fact that the extent of excluded-volume increases markedly with the degree of polymerization (and hence conformational flexibility of the chain) seems to be the cause of the problem.

For low temperature, $x > 1$, the density series for lattice models in general become erratic, but the activity (z) series, which are usually poorly behaved at high temperature,[12] become much better behaved. We do not find this to be the case with the present model.

One approach that we have tried is the use of some nonstandard expansions. We have explored what happens when one expands the modified compressibility as a function of the average degree of polymerization. One finds (letting $\lambda = \langle L \rangle - 1$)

$$2\chi = \lambda - 1\tfrac{1}{2}\lambda^2 + 3\tfrac{1}{2}\lambda^3 - 16\tfrac{3}{4}\lambda^4 + 66\tfrac{1}{16}\lambda^5 - 214\tfrac{1}{16}\lambda^6 + 602\tfrac{3}{16}\lambda^7 - 1387\tfrac{27}{32}\lambda^8 + \ldots \qquad (4.5)$$

The coefficients in this series strictly alternate in sign, and their magnitude increases monotonically. Ratios of successive terms give estimates of the radius of convergence (λ_σ^{-1}); ratios from the fifth term onward extrapolate smoothly to approximately zero. If the extrapolated value is precisely equal to zero, then the radius of convergence of the series is infinite (for example, as it is in the function e^{-x}). The function $\chi(\lambda)$ thus appears to be very well-behaved, but there is no hint of a singulatiy at a finite positive value of λ indicating the onset of sublattice order.

Finally there is a very interesting feature of the high-temperature ($x = 1$) series of (2.2). One notes that the signs of the successive coefficients alternate, except for the glich at $n = 7$. It has been proved[13] that the activity series for hard particle systems must alternate in sign. This holds true for hard particles in continuous space and for lattice gas models of almost any reasonable shape (including rod-shaped molecules, dimers, etc.). In the present model the nature of the excluded-volume effect depends on the coordination of the unit (up to two nearest neighbors are allowed, but more than two are forbidden). In this case the signs in the activity series need not strictly alternate.

Appendix

In this appendix we give the low-density activity series for the model illustrated in Figure 1. We give the coefficients b_n in the activity expansion for the pressure

$$p/kT = \sum_{n=1}^{\infty} b_n z^n \qquad (\text{A-1})$$

We have determined the b_n exactly through $n = 9$ as a function of x, the Boltzmann factor for the interaction between particles. The coefficients are given below.

$$b_1 = 1$$

$$b_2 = -2(1/2) + 2x$$

$$b_3 = 10(1/3) - 16x + 6x^2$$

$$b_4 = -52(1/4) + 118x - 85x^2 + 14x^3 + x^4$$

$$b_5 = 295(1/5) - 872x + 926x^2 - 352x^3 + 22x^4$$

$$b_6 = -1789(5/6) + 6520x - 9144x^2 + 5548(2/3)x^3 - 1214x^4 + 50x^5$$

$$b_7 = 11397(1/7) - 49328x + 85954x^2 - 71856x^3 + 27610x^4 - 3932x^5 + 82x^6$$

$$b_8 = -75238(1/8) + 377040x - 785091x^2 + 836470x^3 - 463095(1/2)x^4 + 121754x^5 - 11517x^6 + 150x^7 - 9(1/2)x^8$$

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$$b_9 = 510609(4/9) - 2906956x + 7040042x^2 - 9114193(1/3)x^3 + 6605145x^4 - 2588428x^5 + 484298x^6 - 32128x^7 + 469x^8$$

References and Notes

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A General Free Volume Based Theory for the Diffusion of Large Molecules in Amorphous Polymers above T_g. 2. Molecular Shape Dependence

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ABSTRACT: The free volume based theory of Mauritz and Storey for the diffusion of extraordinarily large and elongated molecules in rubbery polymers has been generalized in this work to include large molecules of any shape, regular or irregular. As in the original theory, the diffusant molecular hopping displacement is but a fraction of the molecular dimension along a given direction of motion. The accounting for an increase in entropy accompanying the liberation of one penetrant translational degree of freedom after adjacent hole creation, by random thermal fluctuation, has also been retained from our original theory. The basic improvement to the original restrictive model was affected by considering the elementary penetrant diffusive hopping vector to be the vector sum of component displacements along the instantaneous directions of the three principal axes passing through the molecular center of mass. The theory predicts that, for a fixed penetrant molecular volume, compacted structures migrate slower than corresponding extended structures, in qualitative accord with available experimental evidence. Present model shortcomings and suggestions for future improvement are outlined.

Introduction

Mauritz et al. have recently introduced a modified free volume based theory for the above-T_g diffusion of inordinately large molecules in amorphous polymers.[1] In its initial form, the theory was biased toward penetrant molecules having large aspect ratios, which would reasonably be expected to execute hopping primarily along the direction of their long dimensions. Model predictions were roughly compared with available experimental diffusion data for di-*n*-octyl and di-*n*-decyl phthalate plasticizers in PVC. This initial evaluation, although limited in scope, did suggest that a better than order-of-magnitude agreement between experimental and theoretical diffusion coefficients is possible. Assumptions critical to the development of the model were carefully rationalized in the light of suggestions offered by a considerable body of experimental studies of the diffusion of large molecules of various shapes in rubbery polymers. The reader is referred to an earlier paper for a detailed discussion and numerous cited references, which will not be repeated here in the interest of space.[1]

The general equation for the diffusion coefficient for a large and rather elongated molecule of length l, steric volume V_s, and molecular weight M, as derived in our earlier work,[1] is

$$D = (fl/6)(RT/M)^{1/2}\exp((1/2) - fV_s/V_f) \tag{1}$$

where R is the universal gas constant, T the Kelvin temperature, and V_f the average free volume per polymer chain segment in the rubbery state at a given fixed temperature and concentration of diffusant. The simple linear equation of Fujita and Kishimoto[2] relating V_f to temperature and concentration is commonly employed but this will not be of direct concern in the following derivation. The familiar multiple of 1/6 in the exponential prefactor is due to a reasonable assumption of noncorrelated consecutive penetrant jumps in three dimensions as a consequence of the continual and rapid realignment of the penetrant molecule that is surrounded by fluid polymer chain segments. The 1/2 in the exponent, which is not present in the corresponding equation in the conventional free volume theory,[3a] accounts for the liberation of one penetrant translational degree of freedom after adjacent hole creation by random thermal fluctuation. The quantity reflective of the diffusion of particularly large molecules is f, the fraction of the long dimension

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