The graph-like state of matter VII. The glass transition of polymers and Hamiltonian walks

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Abstract. The sensitivity of the Gibbs–DiMarzio theory for the glass transition of polymers to its basic assumptions is analysed. The underlying model, and all the problems it raises, are graph-theoretical in nature. It is shown that the value of the flexing energy parameter ϵ calculated from a measurement of the glass transition temperature T_g, is dominated by the result appropriate to the limiting case when the concentration of holes is zero, the number of chains unity, and the chain length goes to infinity. Accordingly, the problem is dominated by the classical Hamiltonian-walk problem on a lattice graph. An application of known and new results on the enumeration of Hamiltonian walks shows that ϵ is only a semi-empirical parameter at present, and the formal evaluation of ϵ to 1% accuracy is not justified. However, the doubts recently cast on the verifiability of the transition T_2 of the Gibbs–DiMarzio equilibrium theory on various grounds are not considered justified.

The role of the graph-theoretical ingredients of the problem, namely the nature of the lattice graph, its coordination number, and the boundary conditions, are examined. The dimensionality of the embedding space (e.g. the distinction between 'two-dimensional' and 'three-dimensional' lattices) is discarded in favour of the parameter actually relevant, called the r-degree of the lattice graph. Asymptotic results on the enumeration of Hamiltonian walks are presented for the unoriented honeycomb, and for the oriented square and other lattices, including the covering lattices of certain orientations of the diamond and cubic lattices.

1. Introduction

In this series of papers (for the preceding part see Gordon *et al* 1976), the concept of perfectly flexible or 'graph-like' particles for approximate treatments of physical and chemical properties of diverse amorphous materials has been the unifying theme. Models using such particles have a wide currency in the literature, e.g. the random-flight chain in polymer science. The theoretical problems posed and sometimes solved in this connection are rarely recognized for what they are, namely problems in graph theory. This is surprising because the same graph-theoretical notions constantly recur, for instance spanning trees and the special case thereof constituted by Hamiltonian walks (see below); moreover, related problems and notions feature prominently in the relevant branches of the purely mathematical literature. The present paper illustrates this state of affairs by turning attention to the case of glass-like polymers, not previously considered in this series.

In our view, the model of Gibbs and DiMarzio (1958a, b, Gibbs 1956) briefly sum-marized in the following section (§ 2), is the best available for treating the statistical

mechanics of the glass transition, and to serve as a starting point for kinetic treatments also (cf. Adam and Gibbs 1965). Our purpose is to show that a well defined, and actually quite famous, graph-theoretical problem constitutes a limiting case of the problem solved by Gibbs and DiMarzio, and that this limiting case dominates the concrete application to calculations of glass transition temperatures (T_g). Two basic combinatorial approximations have been employed by Gibbs and DiMarzio to estimate the total number of configurations of the system. The first of these is the Flory–Huggins approximation which assumes random occupation of neighbour sites and the second is that of Huggins (1942) which takes into account also the effect of second-neighbour sites. The actual situation seems to lie between these two approximations. The weakness of the approximations used in solving the problem does not throw doubt on the soundness of the model itself in describing the equilibrium properties of polymers near their glass transition. Henceforth we shall refer to a simplified version of the Gibbs–DiMarzio model in which the first of the above mentioned approximations is employed. Recent attacks on the relevance of equilibrium properties to this transition are examined in the discussion (see § 3.1), where the graph-theoretical aspects of the Gibbs–DiMarzio model are then detailed. The most important questions here are the possible effects of the coordination number (§ 3.2.1), of the boundary conditions (§ 3.2.3), of the type of lattice graph, and of the r-degree of points in this graph (§ 3.2.2). The r-degree of a lattice graph is introduced as a function whose properties determine effects usually attributed by physicists to the number of dimensions of the embedding space.

The final paragraph (§ 3.3) of the discussion summarizes the consequences of the results in this paper.

2. The Gibbs–DiMarzio model

In discussions of the entropy of polymer solutions it is usual to employ an expression of the Flory–Huggins type. With suitable generalizations this formula was adapted by Gibbs and DiMarzio to yield a model for the glass transition in polymers. In this treatment n_1 solvent molecules are replaced by n_1 holes. We are then in a position to calculate the number of ways P in which n_1 holes and n_2 chains each comprising x segments can be accommodated on a lattice of N sites. In discussing the glass transition in polymers, a diamond lattice of N sites is employed. We have

$$N = n_1 + n_2 x. \tag{1}$$

The stiffness of the polymer chain is measured by introducing a parameter f. Thus a fraction f of the bonds in the chains on the lattice occur in a *gauche* conformation (energy ϵ) and a fraction $(1-f)$ in the *trans* conformation energy (energy 0). Flory's formula reads

$$P = \frac{N! \, 2^{n_2 + f n_2(x-2)} [n_2(x-2)]!}{n_1! \, n_2! \, N^{n_2(x-1)} [f n_2(x-2)]! [(1-f)n_2(x-2)]!} \tag{2}$$

where P is now the number of ways n_2 chains (each of x segments) can be accommodated on a lattice of $N = n_1 + n_2 x$ sites in such a way that $f n_2(x-2)$ out of $n_2(x-2)$ bonds are in the *gauche* conformation. The behaviour of the parameter f as a function

of temperature T is found by minimizing the Gibbs free energy, thus

$$f = \frac{2 \exp(-\epsilon/RT)}{1 + 2 \exp(-\epsilon/RT)}.$$ (3)

The glass transition temperature T_g is taken to occur when $P = 1$. In terms of ϵ, and the volume fraction v_1 of holes

$$v_1 = n_1/(n_1 + n_2 x)$$ (4)

and v_2 of polymer

$$v_2 = 1 - v_1.$$ (5)

This leads to the following equation for T_g (neglecting a small term $n_2 \ln v_2$):

$$\frac{\ln P}{n_2(x-2)} = 0 = \left(\frac{-1}{x-2}\right)\left(\frac{v_1 x}{1-v_1} \ln v_1 - \ln(2x) + (x-1)\right)$$

$$+ \left(\frac{2 \exp(-\epsilon/RT_g)}{1 + 2 \exp(-\epsilon/RT_g)}(\epsilon/RT_g) + \ln[1 + 2 \exp(-\epsilon/RT_g)]\right).$$ (6)

The diamond lattice has a coordination number $z = 4$, and in general, for a lattice with a general coordination number z, equation (6) can be written in the form

$$\frac{\ln P}{n_2(x-2)} = 0 = \left(\frac{-1}{x-2}\right)\left(\frac{v_1 x}{1-v_1} \ln v_1 - \ln(\tfrac{1}{2}zx) + (x-1)\right)$$

$$+ \left(\frac{(z-2) \exp(-\epsilon/RT_g)}{1 + (z-2) \exp(-\epsilon/RT_g)}(\epsilon/RT_g) + \ln[1 + (z-2) \exp(-\epsilon/RT_g)]\right).$$ (6′)

Equation (6) was used by Gibbs and DiMarzio as well as several other workers (e.g. Beevers and White 1960, Cowie and Toporowski 1968) to fit experimental data on the dependence of T_g of various polymers on the chain length x. Figure 1 is a typical plot, taken from the work of Cowie and Toporowski on α methyl styrene. The chain stiffness parameter ϵ, derived from f by equation (3), has generally been deduced to an accuracy of about 1% (or 0·01 kcal mol^{-1}). No doubt because of the relative complexity of equation (6), an adequate discussion of the sensitivity of such results to the underlying
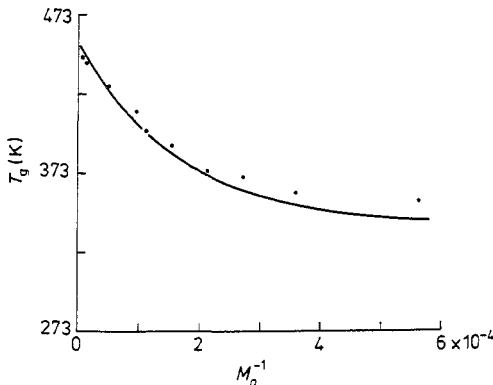

Figure 1. Fit of equation (6) ($\epsilon/k = 610$ K, $v_1 = 0\cdot041$) to T_g as function of chain length of syndiotactic α-methyl polystyrene by Cowie and Toporowski (1968).

assumption has not been given. We show below that a simple analysis is possible. It then emerges that the theory based on the crude Flory–Huggins approximation, as expressed in equation (6'), makes T_g strongly dependent on the coordination number (see equation (18) and § 3.2.1). More seriously, the absolute values of T_g calculated are then appreciably changed, or in practice the measured T_g leads to hefty changes in the flexing energy ϵ employed as an adjustable parameter.

2.1. *Examination of equations* (6) *and* (6')

The object of this section is a critical examination of equations (6) and (6'). The right-hand sides of both, which in effect determine the glass transition temperature T_g, depend on n_2 (the number of chains) only implicitly through the volume fraction $v_1(= n_1/(n_1 + n_2 x))$ of holes. Accordingly in the limit $v_1 \to 0$ the glass transition temperature becomes independent of n_2. The thermodynamic limit requires $N = (n_1 + n_2 x) \to \infty$, but this may be simply satisfied by letting $x \to \infty$. As long as the 'mean field' character of the Gibbs–DiMarzio model is maintained it does not actually matter whether $n_2 \to \infty$ or $n_2 =$ constant as long as $v_1 \to 0$ and $x \to \infty$. One would therefore feel justified in assuming $n_2 = 1$, i.e., only one polymer chain as the system under investigation.

With this assumption following step by step the procedure followed by Gibbs and DiMarzio, we may still obtain equations (6) and (6') (i.e. $x \to \infty$ in equation (6)). Next, using the further limit $v_1 \to 0$, equation (6') becomes:

$$\frac{\ln P}{N} = \frac{(z-2)Q}{\exp(Q)+(z-2)} + \ln\left(1+\frac{z-2}{\exp(Q)}\right) - 1 = 0 \tag{7}$$

where Q is the dimensionless variable

$$Q \equiv \epsilon/RT_g. \tag{8}$$

Furthermore equation (7) would be obtained from equation (6') upon the direct substitutions $n_1 = 0$, $n_2 = 1$, and letting $x \to \infty$. In this latter case the number of configurations of the system (which determines the configurational entropy) equals the number of Hamiltonian walks employed for the packing of the polymer chain(s)—i.e., there is a one-to-one correspondence between polymer configurations and Hamiltonian walks.

Thus, if the following limit exists for the number H_N of Hamiltonian walks:

$$\lim_{N \to \infty} (H_N)^{1/N} \equiv n_H \tag{9}$$

we may, following the probabilistic arguments of the Gibbs–DiMarzio model, and taking into account that the number of available configurations is restrained by (9), show that equation (7) should now read:

$$\frac{\ln P}{N} = \frac{(z-2)Q}{\exp(Q)+(z-2)} + \ln\left(1+\frac{z-2}{\exp(Q)}\right) - \ln\left(\frac{z-1}{n_H}\right) = 0. \tag{10}$$

Finally a rigorous relationship exists between the number of closed-packed ($n_1 = 0$) polymer arrangements on a lattice and H_N which goes beyond the obvious one-to-one correspondence in the case where $n_2 = 1$.

Consider a regular lattice of N points and coordination number z and let $C_{x,N}$ denote the total number of arrangements of $n_2(= N/x)$ x-mers filling the lattice

(assuming that N is an integer number of x). Obviously any Hamiltonian walk can be disconnected to yield a unique x-mer configuration, on the other hand not every x-mer configuration can be converted into a Hamiltonian walk by connecting the end points of the x-mers. Thus by noting that $(N/x) - 1$ end-point connections must be made in order to convert (if possible) the x-mer configuration to a Hamiltonian walk and that each of these connections can be made in certainly not more than $(z - 1)$ ways we obtain the following:

$$(2N/x)(z-1)^{(N/x)-1} C_{x,N} \geqslant H_N \tag{11}$$

where the term $(2N/x)$ accounts for the number of starting points. Thus provided that the following limits exist, we find:

$$\lim_{x\to\infty} \lim_{N\to\infty} (C_{x,N})^{1/N} \geqslant n_{\mathrm{H}}. \tag{12}$$

It is plausible that (12) holds as an equality for lattice graphs of physical interest. We shall put forward the conjecture for all commonly used lattices including the diamond and cubic lattices:

$$\lim_{x\to\infty} \lim_{N\to\infty} (C_{x,N})^{1/N} = n_{\mathrm{H}}. \tag{13}$$

In any case, it is clear that equation (10) may be used to evaluate an important limiting case of the Gibbs–DiMarzio model in terms of the enumeration of Hamiltonian walks, either using the equality, or the inequality sign in equation (12) (to obtain a lower bound for the entropy).

2.2. The Hamiltonian-walk problem

The combinatorial puzzle described above for the Gibbs–DiMarzio model degenerates in the limiting case discussed in the previous section, to a classical graph-theoretical problem: the number of distinct Hamiltonian walks (as distinct from closed Hamiltonian circuits) on a lattice graph. A Hamiltonian walk visits every point of the lattice exactly once. Figure 7 shows some examples of Hamiltonian walks on hexagonal (plane) lattice graphs of various numbers N of points. Our interest is in the asymptotic behaviour as $N \to \infty$ of the number of distinct Hamiltonian walks that can be drawn on any given lattice. No exact and general solution is known, but we shall refer to a famous solution of Kasteleyn (1963a, 1967) for the square lattice, and the new but simple solution for the honeycomb lattice (cf. appendix).

Consider a walk of N steps on a lattice graph of coordination number z for interior points. If the boundary can be neglected, we may consider that all $N + 1$ points of the walk are in the interior. If the restriction of visiting each lattice point only once is given up (i.e. self-intersecting walks are allowed, or the excluded volume effect is neglected), then there are of the order of $(z - 1)^N$ distinct walks of length N from a given lattice point. Using all N starting points, there are

$$P \sim N(z-1)^N/2 \tag{14}$$

distinct walks. The configurational entropy of the system is

$$S_{\mathrm{conf}} = kN \ln(z-1) + k \ln N - k \ln 2. \tag{15}$$

The entropy must become proportional to N as $N \to \infty$, if it is to represent an extensive property of state. It does so and the proportionality constant is

$$\lim_{N \to \infty} S/Nk = S_{\text{conf,mol}}/R = \ln(z-1).$$
(16)

Thus the trivial factor $\frac{1}{2}N$ in equation (14) does not contribute to the entropy and is neglected in the sequel. The reduction in $S_{\text{conf,mol}}$ due to the excluded volume effect, i.e. the elimination of all self-intersecting walks, is estimated from the Flory–Huggins model by passing to the limit $Q \to 0$ in equation (10) (cf. Meares 1965, Vrij and van den Esker 1972). Thus

$$P = [(z-1)/e]^N$$
(17)

and

$$S_{\text{conf,mol}}/R = \ln[(z-1)/e].$$
(18)

2.2.1 The honeycomb lattice. The crudity of this approximation is apparent if we re-derive the limit directly from the assumptions of the Flory–Huggins model (following Gordon 1965). According to equation (14), P varies asymptotically as $(z-1)^N$, if self-intersecting walks are allowed. The multiplying factor required for reducing this result to non-intersecting walks only, is merely approximated by taking it from the case of a polymer chain totally disconnected into monomer units, i.e. N 'walks' of length zero. Then the chance that N points chosen (for these 'walks') on a lattice of N points should all be distinct is $N!/N^N$ ($=$ favourable over total number of selections). By Stirling's approximation this does indeed reduce P by the factor e^{-N} as in equation (17). But we must not conclude that this approximation is as good as Stirling's is in general. We see immediately, for example, that in the special case $z = 3$, equation (17) predicts that P tends exponentially to zero, while it is shown in the appendix that for the concrete example of the honeycomb lattice (figures 6, 7) the exact solution is $P \to \infty$. Physically, however, this turns out to be a minor discrepancy, and the result for $z = 3$ actually lends support to the treatment of the model. This is because the molar entropy, according to (18), turns out to be negative for $z = 3$, and must thus be taken as zero (i.e. the polymer chain will have at least one configuration available to it). And the exact result, given in the appendix, also leads to zero entropy, because P tends to infinity rather weakly, namely like $(\text{constant})^{N^{1/2}}$. To get a meaningful non-zero molar configurational entropy requires that $P \sim (\text{constant})^N$, and this occurs for $z \geq 4$ both in the Flory–Huggins approximation, and as far as is known, in exact calculations for unoriented lattices (see § 2.2.2).

2.2.2. The square lattice. The asymptotics of the enumeration of Hamiltonian walks for $z = 4$ is graph-theoretically more difficult than for $z = 3$. An elegant and exact solution was obtained explicitly for the configurational entropy of chains by Kasteleyn (1963) for a square lattice. He simplified the problem by introducing a specific traffic regulation. Since the Hamiltonian walk arrives at a given lattice point by one line, it has, in principle, $z - 1 = 3$ lines available for continuing to a neighbouring point, but the traffic regulation excludes one of these three, namely, Kasteleyn stipulated that the square lattice was 'oriented' by a system of alternating one-way streets in force in Manhattan. This move was motivated by mathematical simplicity but could, in principle, be justified by reference to bond angles. (The restriction of the chain to a course consistent with the Manhattan traffic flow is not easy to translate into bond angle restrictions, but a more

convincing case, that of the corresponding 'covering lattice', is also mentioned by Kasteleyn. In that case, (included in table 1), at each corner, the walk must continue at right angles—either to the left or to the right—so that the bond angle is restricted to 90°.) The computational difficulty of the boundary effects (cf. § 3.2.3) arising with a finite square lattice is much reduced by the choice of toroidal boundary conditions, i.e. the square lattice is imagined to be embedded in the surface of a torus without any free boundary edges. The exact asymptotic solution of the graph-theoretical problem of the number of Hamiltonian circuits for a square lattice on a torus derived by Kasteleyn is:

$$P \sim \exp(CN/\pi) \sim 1 \cdot 338^N \sim e^{0 \cdot 292N} \tag{19}$$

where C is Catalan's constant

$$C = 1 - (\tfrac{1}{3})^2 + (\tfrac{1}{5})^2 - \cdots \sim 0 \cdot 916. \tag{20}$$

In comparing the exact result of equation (19) with that of the Flory–Huggins approximation usually employed, one must bear in mind that the latter refers to a lattice unrestricted by traffic regulations (i.e. to unoriented graphs). Accordingly equation (19) gives a lower bound for the more general unrestricted problem. It may seem reasonable to expect that for the unrestricted case P varies as the Nth power of a constant larger than $1 \cdot 338$, since a walk can then continue, in principle, in three rather than two directions at each site. Domb (1974) pointed out that the result obtained by Lieb (1967) and Lieb and Wu (1972) for the residual entropy of 'square' ice forms an upper bound to n_H for the case of an unoriented square lattice, i.e. $n_H < 1 \cdot 539$. Orr (1947) estimated $n_H \simeq 1 \cdot 4$ for the same case. Furthermore, one of us (AM) has carried out enumerations on a computer; these provide an estimate of $n_H = 1 \cdot 38$, with limits $\pm 0 \cdot 042$ suggested by reference to the lower bound of $1 \cdot 338$ provided by Kasteleyn's result for the unoriented lattice. It seems not unlikely this lower bound coincides with the exact solution, notwithstanding the traffic regulations imposed by orienting the lattice. The limit of the Flory–Huggins result gives only

$$P \sim (3/e)^N \sim 1 \cdot 104^N. \tag{21}$$

The comparison of the lower bound of $1 \cdot 338$ with the estimate of $1 \cdot 104$ is not favourable as is seen by calculating the corresponding entropies per site, namely, from equation (19)

$$S/kN = (\ln P)/N = 0 \cdot 292 \qquad \text{(lower bound)} \tag{22}$$

and from equation (21)

$$S/kN = (\ln P)/N = (\ln 3) - 1 = 0 \cdot 099 \qquad \text{(limit of the Flory–Huggins approximation).} \tag{23}$$

There is thus an error of at least about a factor of three in the entropy calculated for the square lattice from the Gibbs–DiMarzio treatment based on equation (23). The same is likely to be true for the diamond lattice (see § 3.2.2). In fitting the model to the measured chain length as a function of x, any such error has been compensated successfully by adjusting the enthalpy parameters ϵ and (occasionally) v_1. We now show that, as might be expected, such artificial adjustments are large enough to render the comparison of the resulting ϵ with rotational barriers inaccurate. To this end we write the first equality of equation (7) in the form (using $z = 4$)

$$(\ln P)/N = [2Q/(2 + \exp Q)] + \ln[1 + (2/\exp Q)] - 1 \tag{7'}$$

which duly reduces to equation (23) for $Q = 0$. To test the effect of passing to the better approximation of equation (22) we should amend equation (7') according to equation (10). We thus obtain (using $n_H = 1 \cdot 338 \ldots$)

$$(\ln P)/N = 2Q/(2 + \exp Q) + \ln[1 + (2/\exp Q)] - 0 \cdot 807. \tag{10'}$$

According to equation (7), the glass transition temperature is determined by equating the right-hand sides of equation (7') or equation (10') to 0, and the result is shown graphically in figure 2. We see, by comparing points A and B, that Q changes by about 50% when the solution to the combinatorial problem is improved by passing from the Gibbs–DiMarzio (Flory–Huggins) model to Kasteleyn's result. The situation is little changed if we do *not* put the free volume fraction $v_1 = 0$, as in equation (7), but retain the term $(v_1 x \ln v_1)/(1 - v_1)(x - 2) \sim v_1 \ln v_1/(1 - v_1)$ from equation (6). The usual value used is $v_1 = 0 \cdot 025$ which yields a term $v_1 \ln v_1/(1 - v_1) = 0 \cdot 0945$ to be added on the right-hand side of equation (7') and (10'), which moves both curves in figure 2 up by the same constant. We note that the whole of the free volume effect usually taken into account amounts to only one half of the difference $(1 - 0 \cdot 807 = 0 \cdot 193)$ between the two approximations to the underlying graph-theoretic problem!
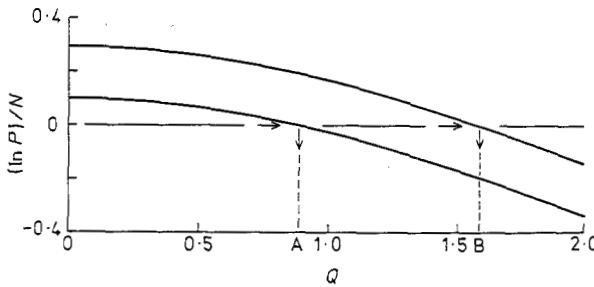

Figure 2. Plot of $(\ln P)/N$ against the parameter Q which measures the bond-flexing energy (equation (8)). The lower plot is according to equation (7), the upper plot according to equation (10). Note the large correction, from A to B, in the flex parameter, as calculated from the measured T_g, where $\ln P$ is equated to zero by the model.

3. Discussion

It was argued by Gibbs and DiMarzio that underlying the slow relaxations observable near a glass transition T_g region, there is a thermodynamic transition which is reflected by their statistical-mechanical model. This temperature which they called T_2, may lie as much as 50° below the observed (and rate-dependent) T_g. The kinetic aspects were later appropriately treated by Adam and Gibbs (1965). However, the experimental verifiability of the *thermodynamic* transition T_2 is periodically called into question. We therefore devote the next section to a review of the thermodynamic evidence.

3.1. Reality of the thermodynamic transition

Rehage and Borchard (1973) gave an excellent summary of the treatment of the glass transition by Gibbs and DiMarzio: 'The usually observed transition to the glassy state is treated as a kinetic process by these authors, but at infinitely slow cooling the transition

temperature should be lowered to such an extent that it coincides with the transition temperature T_2. This would then make the glassy solidification a genuine second-order transition.' We agree with this, but not with the next sentence: 'This model is certainly very useful for the qualitative description of some phenomena, but this transition, purely for experimental reasons, cannot be proved.' Figure 1 exemplifies the way in which the model gives a *quantitative* account of the dependence of T_2 on structural parameters. As regards experimental verifiability, since no measurement at an exact point is possible, all thermodynamic transitions are found experimentally by extrapolation (or interpolation); but the length of extrapolation on the temperature scale, which is necessary in a given case, is not the only factor which governs the proof of existence of a transition. For example, the quasi-linear range covered by the data points is also important; and a good statistical-mechanical model can raise our confidence in a linear extrapolation. In the case of the glass transition, the slowness of relaxations forces us to treat the equilibrium properties by extrapolation from regions of higher relaxation rates, e.g. higher temperatures. In this way, the paradox of Kauzmann (1948) arose from plotting the entropy of a liquid/glass system against temperature. Unless there is a rather sharp change in slope just below the observed freezing in of the motions, the entropy of the glass would soon fall below that of the crystal, in violation of the third law. The situation becomes specially clear if the plot is linearized in the usual way (figure 3).
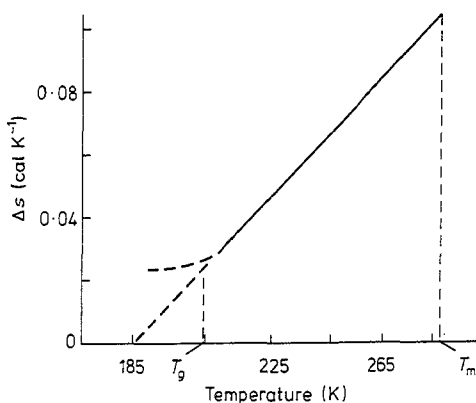

Figure 3. Difference in molar entropy between liquid and solid D-L lactic acid re-plotted against $0.6519 \lg T - 0.000216 T$. This procedure converts the plot by Kauzmann to a straight line for better extrapolation. Unless a marked change of slope occurred (as shown by the broken curve) in the slow-relaxation region at low temperature, the third law would be violated, since the entropy of the supercooled liquid would be negative at absolute zero (from Gordon 1965, following Kauzmann 1948).

Rehage and Borchard presented two methods of constructing equilibrium volumes of polystyrene below the T_g, i.e. below the temperature at which vitrification occurs on slow cooling. We reproduce the relevant features of the two figures concerned (their figures 14 and 15; our figures 4 and 5 respectively). In each case, they argued that these two equilibrium curves give 'no indication of a transition'. In our opinion, our figure 4 shows the expected result and no theory would predict any other, while figure 5 actually supports the existence of T_2.
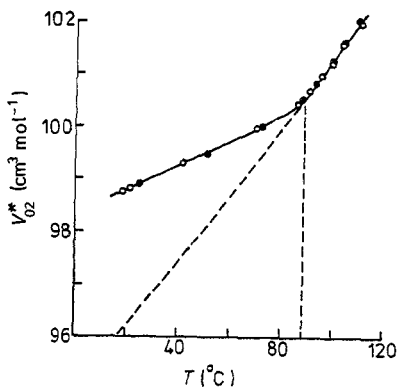
Figure 4. Plots of volume per base mole of atactic polystyrene (M_n = 20 000) melt (full line) and partial molar volume of the polymer in diethyl malonate (broken line) as functions of temperature, after Rehage and Borchard (1973).
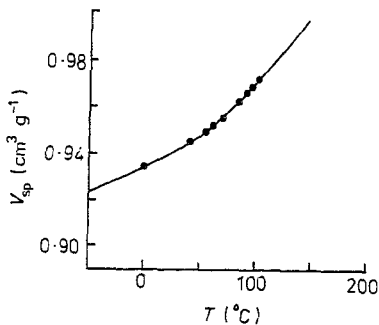

Figure 5. Plot of specific volume of polystyrene as function of temperature constructed by Rehage and Borchard (1973), by a procedure depending on measurements at various pressures.

In detail, figure 4 represents their data for bulk polystyrene in the melt and the glassy states (full lines), and the partial specific volume of the same polymer in diethyl malonate (the slightly curved broken line). While this extends the findings of Heller and Thompson (1951) to solutions of higher concentrations, all solutions used for figure 4 were still in the liquid state (not glassy), and therefore no kink is expected in the broken line (see also Gordon and Taylor 1952). The Gibbs–DiMarzio model shows clearly why T_2 is depressed by the presence of solvent.

Nor does figure 5 disprove the existence of a thermodynamic transition but it rather supports it. Its authors say merely: 'this curve shows a wide curved course on which one cannot very well distinguish a kink point.' It is not the case that the existence of a seond-order Ehrenfest transition is predicated on an absolutely sharp kink, and what rounding is actually observed lends additional interest to theoretical interpretations. Where two essentially linear portions of a thermal expansion curve are separated by a rounded portion, the experimentalist is apt to extrapolate the linear portions to meet at a fictitious point which to him represents T_g. The theoretical sanction for this time-honoured procedure is simple: thermodynamics guarantees that the fictitious point would respond to variables like pressure etc. precisely in the same way as a 'real'

infinitely sharp kink, provided the system is characterized by a single-disorder parameter. The situation is well understood in other branches of physics. For instance, Kazantsev and Surdutovich (1974) describe the transition of a laser to a self-sustained operation as an oscillator as a second-order phase transition. (Unfortunately, in chemistry the word 'phase' is reserved for first-order transitions, i.e. the case where two distinct 'phases' are in equilibrium.) They show a theoretical plot with a sharp kink, calculated from an infinite-volume model, of E^2 against $N/N_{threshold}$, where N is the number of excited atoms and E the energy radiated. A more refined quantum-theoretical model leads to a 'blurring' of the transition, and is more realistic. But they do not argue that the local rounding of the curve should lead us to abandon the description in terms of the 'unblurred' Ehrenfest transition. The construction of figure 7 by Rehage and Borchard, from their careful measurements, provides an opportunity for future refinements of the T_g theory. The finite volume of a real sample would probably lead to a less pronounced rounding of the curve than is observed here; nor does it seem likely that quantum effects (e.g. tunnelling through rotational barriers) would contribute sufficiently strongly. The proper interpretation of the observed 'blurring' is still open in this case.

Finally, Haward's (1975) restriction of thermodynamic second-order transitions to the more frequently realized subclass in which the heat capacity undergoes a step in the direction opposed to that at T_g, is unwarranted.

3.2. The graph-theoretical basis of the Gibbs–DiMarzio model

While this work was in progress, an important paper by Nagle (1974) appeared, which deals with the first-order melting transition of polymers, but incidentally makes explicit the connection between the combinatorial entropy of the Gibbs–DiMarzio model and graph theory. This combinatorial entropy contributes to the free energy from which both first-order (melting) and second-order (glass) transitions are calculated in different ways, but this distinction is not explicitly pointed out in Nagle's paper. The relevance of Kasteleyn's result was mentioned in a footnote to his paper, and the sensitivity of the model to the combinatorial approximation was clearly brought out. The limit we calculate for the Flory–Huggins approximation (our equation (17)) can be obtained also from his equation (7.3). Moreover, he gives a separate limit (his equation (7.8)) for the improved second-approximation treatment of the combinatorial problem by Huggins (1942). It emerges that this Huggins approximation gives a substantially larger combinatorial entropy in the high-density limit ($v_1 \rightarrow 0$), namely our equation (17) becomes:

$$P = \{(z-1)/[z/(z-2)]^{\frac{1}{2}(z-2)}\}^N \tag{24}$$

which, for coordination number $z = 3$, gives an overestimate of $P \sim 1 \cdot 15^N$ (instead of unity) and for $z = 4 : P \sim 1 \cdot 5^N$ (instead of $1 \cdot 104$ by Flory–Huggins, equation (21)). Although this result of $P \sim 1 \cdot 5$ appears to be an overestimate quite generally (see table 1), it is definitely a better approximation for the Gibbs–DiMarzio model than the crude Flory–Huggins approximation $P \sim 1 \cdot 104^N$. Unfortunately, data fitting in the literature has generally been based on this latter approximation, perhaps because originally Flory expressed his view that the inclusion of the Huggins term was hardly worthwhile. We must, however, bear in mind that Flory was thinking of dilute solutions ($v_1 \sim 1$), whereas it now emerges that for the limit $v_1 \sim 0$ in the glass transition theory, Huggins's expression is very significantly different (table 1).

Table 1.

Specification of point lattice	z^a	$\bar{z}^a$	n_H	Flory–Huggins approximation (see equation (17))	Huggins approximation (see equation (24))
1. Honeycomb lattice (unoriented, figure 7)	3	—	1^b	0·735	1·15
2. Square lattice oriented in accordance with the Manhattan orientation (figure 8)	4	2	$1·338515\ldots^c$	1·104	1·5
3. Square lattice oriented in accordance with the underlying orientation of the Manhattan orientation (figure 9)	4	2	1^d	1·104	1·5
4. Covering lattice of the Manhattan-oriented square lattice (figure 10)	4	2	$1·3758\ldots^e$	1·104	1·5
5. Covering lattice of an oriented diamond lattice (figures 11(a), (b))	4	2	$1·398 \pm 0·002^f$	1·104	1·5
6. Covering lattice of an oriented cubic lattice (figures 12(a), (b))	6	3	$1·810 \pm 0·002^f$	1·84	2·22

a z = coordination number where $\bar{z}$ = out degree, i.e. number of outgoing lines.
b See appendix.
c Kasteleyn (1963a).
d Extrapolated computer results (to be published). (The corresponding lattice (figure 9) with free edges is not Hamiltonian.)
e Exact result (to be published).
f Computer results (to be published): extrapolation, using periodic boundary conditions.
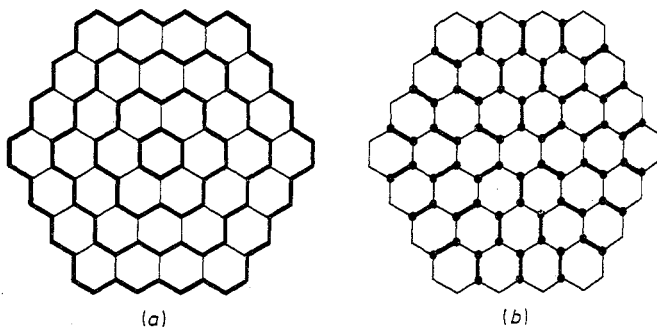

Figure 6. Classification of lines in honeycomb lattice into tangential (shown bold in (a)) and radial (bold in (b)).

3.2.1. The coordination number z. Although all other *pseudo*lattice theories (see Tompa 1956) for amorphous polymer systems are required to be insensitive to changes in the coordination number z, the Gibbs–DiMarzio theory has been treated, probably with justification, as an exception. The assumed diamond structure, disordered by
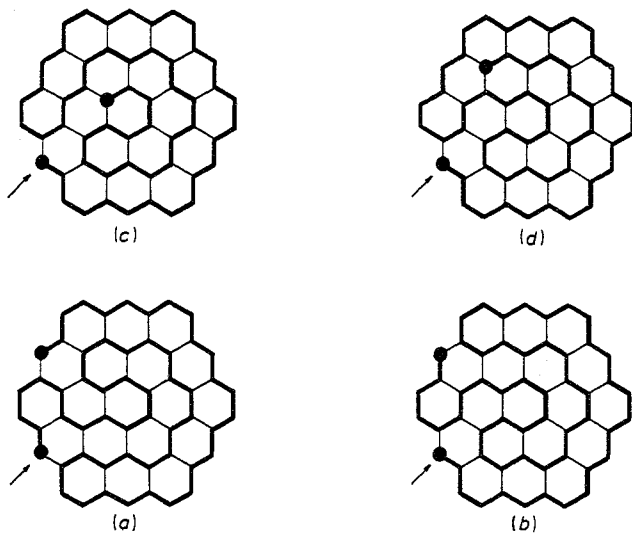
Figure 7. Various Hamiltonian walks (bold lines with end points marked) on honeycomb lattice of $L = 3$ layers of hexagons each.
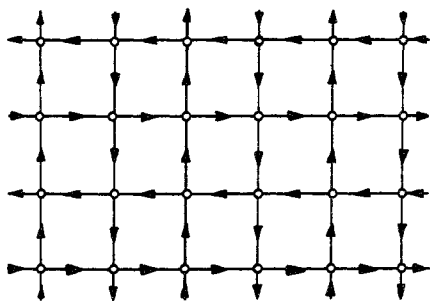

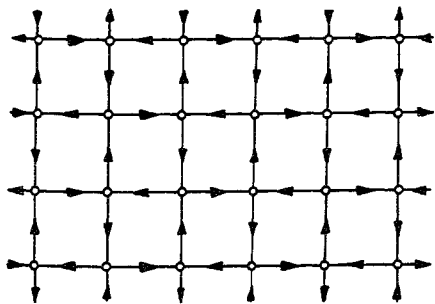**Figure 8.** The Manhattan closed oriented square lattice. (Following Kasteleyn (1963).)

Figure 9. Square lattice oriented in accordance with the underlying orientation of the Manhattan-oriented lattice (i.e. the underlying lattice of the Manhattan-oriented lattice with diagonal boundary conditions (lines)).
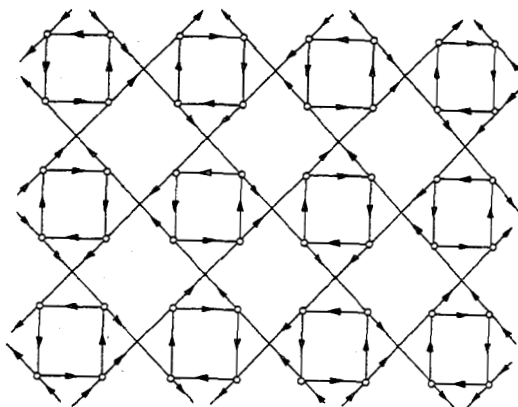
Figure 10. Covering lattice of the Manhattan-oriented lattice. (Diagonal boundary conditions (lines) are again assumed on the Manhattan-oriented lattice.)

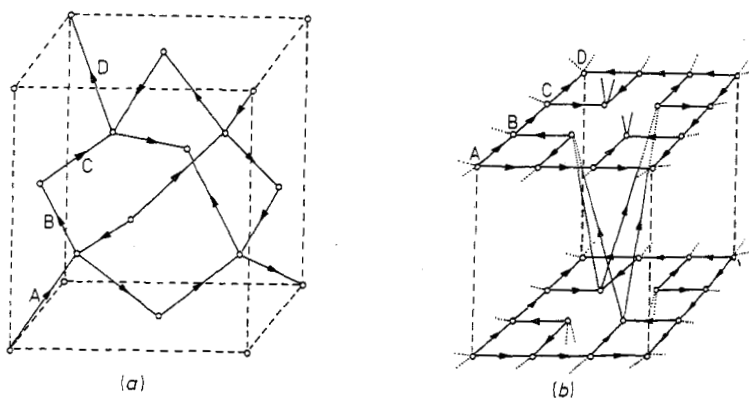(a)   (b)

Figure 11. (a) Unit cell of a closed oriented diamond lattice. (b) Covering lattice of the oriented diamond lattice. Motif picked out (with some distortion) to illustrate the structure of the closed oriented lattice. (The true unit cell has 16 crystallographic points; the motif shown comprises 9 such points, e.g. the 8 at the corners of the cube are counted as one, because their weight = 1/8). The points marked A, B, C, D correspond to the lines so marked in (a) under the construction of the covering lattice.

breaking about half of the C—C bonds, does justice to the conformational properties of the polymer backbones. The fact that the coordination number $z = 4$, involved in this model, underestimates the number of neighbour segments belonging to other chains, is presumably unimportant, because intermolecular interactions are adequately taken care of by the assumption of a fraction of lattice vacancies (holes). Table 1 presents results of computer calculations for various lattice types, to be published in more detail later, which show that the dependence of the configurational entropy depends primarily on z, in a manner approximately foreshadowed by the customary crude approximation of Flory–Huggins. However, when the crude approximation is abandoned for more exact calculations, minor variations become apparent, and are discussed below, for lattices of different type but constant z. The results in this table concern of course, the limiting case ($n_1 = 0$, $n_2 = 1$, $x \to \infty$). This limit has been shown in § 2.1 to dominate the result of calculating T_g from the theory, and it is hardly likely that our conclusions
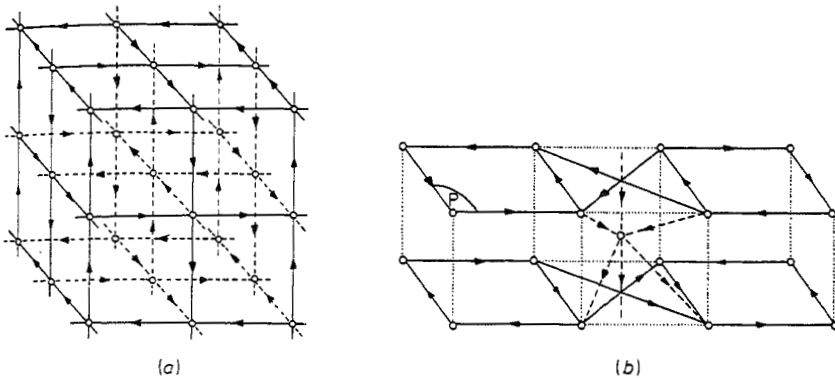
Figure 12. (*a*) A closed oriented cubic lattice. (Note that the *X–Y*, *X–Z* and *Y–Z* planes are Manhattan-oriented square lattices, therefore we may call this lattice 'Manhattan-oriented cubic lattice'.) (*b*) Covering lattice of the Manhattan oriented cubic lattice. Motif picked out to illustrate the structure of the closed oriented lattice graph. The plane marked P is oriented in the same manner as the oriented lattice in figure 10 and may correspond to any *X–Y*, *X–Z* or *Y–Z* plane of the underlying lattice in (*a*), under the construction of the covering lattice. Dotted lines do not belong to the lattice graph; they are merely drawn to clarify spatial relationships.

would be affected by the small term depending on $v_1 > 0$ and the correction for $x < \infty$ present in practice, nor by the adoption of $\epsilon > 0$ which is of course necessary for a finite T_g to be calculated.

3.2.2. Type of lattice graph and the dimensionality of the embedding space; the r-degree of the graph.

There are problems going beyond the effect of the value of the coordination number, which can be discussed in the light of table 1. The type of lattice graph to be assumed, and the dimensionality of the space in which such a graph is efficiently embeddable (so as to achieve translational symmetries consonant with constant bond lengths etc), are problems of interest to theoreticians. The problem of enumerating Hamiltonian walks, which has been shown to represent the limiting case of the Gibbs–DiMarzio model and to dominate its quantitative results, is seen in table 1 to be relatively insensitive to lattice type or to dimensionality of the notional embedding space, as long as the coordination number is kept constant and (examples 2, 4, 5), as long as artificial traffic restrictions are avoided (example 3). In the problem of finding the number C_n of self-avoiding walks of n steps in general (not necessarily those visiting every point of a given lattice), Domb and Sykes (1961) found variations in $\mu(\equiv \lim_{n\to\infty}(C_n)^{1/n})$ with the dimensionality of the embedding space, which were considered to be significant. These variations are exemplified (Sykes *et al* 1972) by $\mu = 4 \cdot 1517$ for the triangular lattice ($z = 6$) and $\mu = 4 \cdot 6835$ for the simple cubic (sc) lattice ($z = 6$), giving the ratio $4 \cdot 6835/4 \cdot 1517 = 1 \cdot 128$. Table 1 shows that the ratio of n_H for the 'three-dimensional' covering lattice of the diamond to n_H for the 'two-dimensional' Manhattan-oriented square lattice is $1 \cdot 398/1 \cdot 339 = 1 \cdot 044$, where the coordination number is $z = 4$ for both lattices. In our discussion the ratio represents a relatively innocuous deviation from unity when compared to the value of $n_H = 1 \cdot 10$ (obtained from the crude combinatorial approximation) hitherto used in fitting data on T_g. As always, the significance of variations due to the artificially assumed lattice type must be weighed in the light of the actual physical theory under discussion.

It must be emphasized that the dimensionality of the embedding space is not the appropriate theoretical tool for analysing the variations. The combinatorial problem relates to a lattice graph, and is quite independent of the dimensionality of the embedding space, of its metric, or of topological problems (like the planarity of a graph) connected with such embedding. To put it crudely, the number of Hamiltonian walks on a square lattice graph embedded in the surface of a torus is invariant to continuous transformations of the toroidal surface, or of tying knots in the torus, but remains a property of an essentially one-dimensional object, namely a graph.

It is well known that random walks on 'three-dimensional' lattices have a finite chance of escaping from the origin for ever, while on a 'two-dimensional' lattice they return to the origin infinitely often. This seems to belie the statement that the number of random walks, like that of Hamiltonian walks, is independent of the dimensionality of the embedding space, and merely a property of the lattice graph. Yet the statement is true, and we propose the following description of the situation. Consider the notion of the degree z of a point in a graph, namely, the number of lines incident thereon. Generalize the notion to that of the r-degree of a given point, defined as the number of points linked to the given point by paths consisting of r lines, and which cannot be reached by paths of less than r lines. Then z is merely the special case $r = 1$, i.e. the 1-degree of a lattice point. Now in the square lattice graph, the r-degree $\propto r$, and in the cubic lattice graph the r-degree $\propto r^2$ for large r. This is the graph-theoretical reason for the different statistical behaviour of the return to the origin in the two cases, as is clear from the usual proofs of the result. The concept of r-degree was used by Kasteleyn (1967) in his elegant proof of Kirchhoff's (1847) theorem for the enumeration of spanning trees, and earlier (Kasteleyn 1963b) he defined the 'dimensionality' of a lattice graph, namely $\lim \ln(r\text{-degree})/\ln r$ plus unity, as an intrinsic property independent of an embedding space.

3.2.3. Boundary conditions. Boundary effects have been neglected altogether in the literature on models for the glass transition. Since the present work shows the Gibbs–DiMarzio model to be largely dependent on the Hamiltonian walk problem, its formal dependence on boundary conditions deserves attention. Consider the honeycomb and square lattice graphs with various boundaries (figure 13). The honeycomb
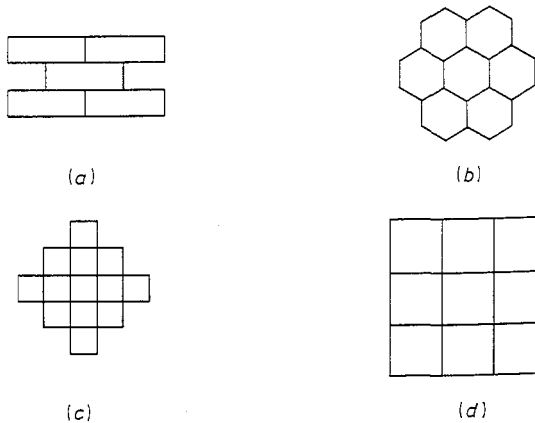

Figure 13. Various boundary conditions: (*a*) brickwork lattice; (*b*) hexagonal lattice; (*c*) layered square lattice; (*d*) square lattice.

lattice can be continuously deformed into the so called brickwork lattice graph, i.e. from the two-dimensional space group $P6mm$ to $C2mm$. The natural boundary conditions, i.e. those affording maximum preservation of symmetry are $6mm$ (figure 13(b)) and $2mm$ (figure 13(a)) respectively. The former gives $H_N \sim c^{N^{1/2}}$ (appendix) and computer results suggest that the same is true for the latter. Computer results on the brickwork lattice with toroidal boundary conditions suggest that H_N is much increased over the free boundary cases of figures 13(a) and (b), but the asymptotic behaviour remains an open problem. We are grateful to a referee for pointing out that figure 13(c) leads to $H_N \sim c^{N^{1/2}}$ and this underlines the danger inherent in neglecting boundary conditions. For the square lattice we can show that the boundary of figure 13(d) leads to $H_N \sim c^N$ (on the assumption of equation (9)) which is the well behaved case.

Actually the Hamilton walk problem forms a lower bound to the x-mer problem. Any sensitivity of the former to rather restrictive boundary conditions by no means necessarily implies a corresponding sensitivity of the x-mer problem.

3.3. Consequences of this investigation

We regard the model of Gibbs and DiMarzio as the best one available for rationalizing the main features of T_g. The number of configurations (or entropy) has been shown to be seriously underestimated by the model, in comparison with exact analytical or near-exact computer results for different lattices. The practical effect of this demonstration would, on the face of it, demand a substantial upward revision of the values of the chain-stiffness parameter, the rotational barrier ϵ. However, when we bear in mind the sensitivity of the entropy to the coordination number of the lattice graph, and other artificial features of the model, it seems mandatory to conclude that ϵ had better be reconsidered as an adjustable parameter which we cannot hope to interpret absolutely in molecular terms. Differences in ϵ values calculated from T_g of similar systems can, no doubt, retain their molecular interpretation in terms of differences in rotational barriers. The situation has its analogy in the semi-empirical status of the single Flory–Huggins parameter χ, which dominates the opposite limiting case of infinite dilution.

The explicit characterization of the whole problem in graph-theoretical terms suggests some routes to further progress. For instance, the model should lend itself to the incorporation of the effect of side groups. These groups have so far been stripped from the backbone, thus reducing the problem to that of self-avoiding lattice walks. We recall that the theory of such walks can be generalized to exclude the approach of two points of the chain to within a given number of lattice steps. In this way, side groups could be accommodated by the theory, and the entropic effects due to side groups of different sizes could be studied. Finally, we draw attention to the need (cf. § 3.1) to account theoretically for any rounding off or blurring of the thermodynamic (Ehrenfest) transition underlying T_g.

Appendix. The number of Hamiltonian walks on a honeycomb lattice

We adopt a hexagonal boundary, enclosing L layers of hexagons, say. Figure 6 shows two examples with $L = 4$; the innermost 'layer' comprises a single hexagon. The lines (line segments) are classified into tangential (figure 6(a)) and radial (figure 6(b)); the radial lines form *ties* between the layers of tangential lines. Figure 7 shows four of many examples of Hamiltonian walks for $L = 3$. In each case, one of the two end points of the walk lies on the outermost layer, and this is unavoidable, since all points on the outer layer could not otherwise be visited by a Hamiltonian walk. Figure 7 also shows that the second end point can occur on any of the tangential layers, and that two end points do not define the Hamiltonian walk (figures 7(a) and (b)).

The number $H(L)$ of distinct Hamiltonian walks for L layers is found as follows. Let $D(L)$ be the number of double-entry Hamiltonian walks (both end points on outer layer), and $S(L)$ the number of single-entry Hamiltonian walks (one end point on outer layer), and proceed by induction on L. For any double-entry walk on L layers, remove the outermost layers of tangential and radial lines, thus generating a double-entry walk on the lattice of $L - 1$ layers. Conversely, each double-entry walk on $L - 1$ layers can be continued outward (at both ends) to produce exactly two distinct walks on L layers:

$$D(L) = 2D(L-1). \tag{A.1}$$

Similarly it is easy to verify that

$$S(L) = 2S(L-1) + 4D(L-1). \tag{A.2}$$

Since $S(1) = 0$, $D(1) = 6$, these recurrence relations are easily solved to yield

$$H(L) = S(L) + D(L) = 3(2L-1)2^L. \tag{A.3}$$

Also, using the easily verified relation for the number N of lattice sites:

$$N = 6L^2 \tag{A.4}$$

we find the number of Hamiltonian walks as a function of N:

$$H(N) = h_N = [(6N)^{1/2} - 3]2^{(N/6)^{1/2}} \tag{A.5}$$

This result fails to yield a finite molar configurational entropy, essentially because the number of Hamiltonian walks varies exponentially with the number L of lattice layers (e.g. equation (A.3)) but not with the number N of sites (e.g. equation (A.5)).

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