Remarks on the Energy Parameters in Lattice Treatments of the Glassy State

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ABSTRACT: The treatment of the glassy state put forward by Gibbs and DiMarzio results in two, independent correlations that might be used to predict the transition temperature T_2 from other observable quantities. It is shown that one of these, involving ϵ/kT_2, where ϵ is a "flex energy", is of little value in predicting T_2 since an appropriate ϵ is not accessible by independent experiment. The other, involving E_0/kT_2, where E_0 is a "hole interaction energy", proves to be interesting owing to a correlation between E_0 and $V_s\delta^2$, where δ is the cohesive energy density and V_s is the segmental volume.

The treatment of the glassy state put forward by Gibbs[1] (and later, Gibbs and DiMarzio[2]) attempts to provide a thermodynamic understanding for some of the properties of the glassy state of amorphous polymers. The calculation employs, with slight modification, a partition function for a polymer chain on a lattice introduced by Flory in another context.[3] The special features of the partition function for the discussion of the glassy state are the inclusion of a flex energy ϵ to weight steps on the lattice and a term n_1E_0/kT corresponding to the van Laar heat of mixing term $n_1\chi_1(T)\phi$ used by Flory. Here ϵ is the energy by which one of the steps on the lattice is preferred over alternative steps, and n_1 is the number of holes (solvent for Flory) with E_0 an interaction energy (since n_1 is small, the solute volume fraction ϕ is set equal to unity in the treatment). The calculation proceeds to use the modified partition function to find the temperature T_2 such that the entropy of mixing of polymer and holes is zero under the stipulation that the difference $(\alpha_l - \alpha_g)$ in thermal expansivities of liquid and glass is proportional to $\partial n_1/\partial T$ for $T > T_2$ (with $\partial n_1/\partial T = 0$ for $T < T_2$). It is the purpose here to point out that from a pragmatic point of view the inclusion of the flex energy ϵ is of little benefit in attempts to correlate data on T_2 with molecular properties and that an interesting relation may exist between E_0 and the cohesive energy density σ^2, permitting, at least in principle, estimation of T_2 from data on δ, α_l, α_g and the molar volume per chain segment.

Before turning to our principal purpose, it should be remarked that a general discussion of the merits or demerits of the treatment of the glassy state utilizing Flory's (modified) partition function in the range of temperatures such that the configurational entropy is (nearly) zero is outside the scope of this paper. For example, specific effects of densification on the local packing that might require ϵ, E_0, or the lattice coordination number z to be functions of temperature will not be considered here,[4] but rather these will be assumed to be constants, in the spirit of the lattice treatment. Our limited purpose is to explore certain ramifications of the results obtained by Gibbs and DiMarzio as they pertain to the prediction of T_2 from independently available estimates of parameters appearing in the treatment.

The Lattice Model

The partition function described above may be used to calculate ϵ/kT_2 and $zE_0/2kT_2$ as functions of $(\alpha_l - \alpha_g)T_2$. The partition function used by Gibbs[5] leads to the relations

$$S_1(\epsilon/kT_2,x,z) + S_2(zE_0/kT_2,x) = 0 \tag{1}$$

$$(\alpha_l - \alpha_g)T_2 = F(zE_0/kT_2,x,z) \tag{2}$$

where x is the chain length. (Of course, these relations are also given in ref 5.) The separation into terms dependent on zE_0/kT_2 and ϵ/kT_2, x, and z is evident. The functions S_1, S_2, and F are given by the following

$$S_1(\epsilon/kT_2,x,z) = \frac{x-3}{x}\left\{\ln(1+Y) + \frac{Y}{1+Y}\frac{\epsilon}{kT_2} + \frac{1}{x}\ln\frac{z(z-1)x}{2}\right\} \tag{3}$$

$$S_2(zE_0/kT,x) = -1 - \frac{V_0}{1-V_0}\ln V_0 + \frac{1}{x}[1 - \ln(1-V_0)] \tag{4}$$

$$F(zE_0/kT_2,x,z) = \frac{\frac{z}{2}V_0\ln q - V_0\ln V_0}{\frac{z}{2}\left(1-\frac{V_0}{q}\right) - z\frac{V_0}{q}\ln q + 2\frac{V_0}{q}\ln V_0 - \frac{z-2}{z}\ln(1-V_0)} \tag{5}$$

where

$$Y = (z-2)\exp(-\epsilon/kT) \tag{6}$$

$$zE_0/2kT_2 = -\left[\ln V_0 + \left(1-\frac{1}{x}\right)(1-V_0)\right] \tag{7}$$

$$q = 1 - \frac{2(1-V_0)}{z}\left(1-\frac{2}{x}\right) \tag{8}$$

Qualitatively similar relations obtain with the slightly different partition function of Gibbs and DiMarzio.[2] The results in Figure 1 were calculated with eq 1–8. In constructing Figure 1, it was convenient to choose V_0 and then (for a given x and z) compute $zE_0/2kT_2$ with eq 7, $(\alpha_l - \alpha_g)T_2$ with eq 2, 5, and 8, and finally ϵ/kT_2 with eq 1, 3, and 4. An iterative method was used to solve for ϵ/kT_2 in the latter case.

The reduced parameter ϵ/kT_2 is shown as a function of $(\alpha_l - \alpha_g)T_2$ in Figure 1a for several values of the coordination number z and chain length x. As mentioned, Figure 1a was calculated with the partition function used by Gibbs.[5] Qualitatively similar results obtain with the slightly different partition function of Gibbs and DiMarzio,[2] the principal difference being that with the latter, values of ϵ/kT_2 are all increased somewhat. (A result similar to that of Figure 1a based on the Gibbs–DiMarzio partition function is given by Eisenberg and Saito[6] for one case ($z = 4$ and $x = \infty$), and additional curves could be constructed by cross-plotting data given by Moacanin and Simha in Figures 1–3 of ref 7. It appears that the term $\phi(E_0/kT)$ of ref 7 is not in accord with eq 22 of ref 2, but the discrepancy is not too important for the range of $(\alpha_l - \alpha_g)T_2$ of interest here.)

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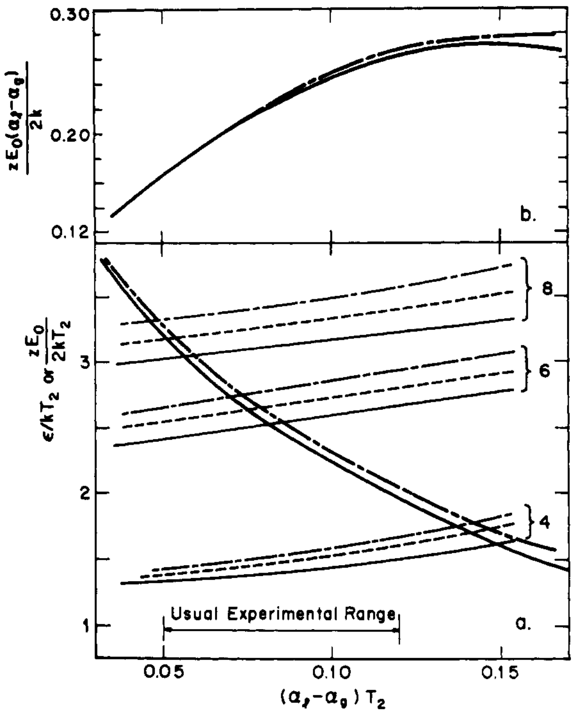

Figure 1. Curves calculated with the Gibbs-DiMarzio lattice model: (a) bold curves, $zE_0/2kT_2$ vs. $(\alpha_l - \alpha_g)T_2$ for infinite chain length (solid curve) and $x = 20$ (chain curve); light curves, ϵ/kT_2 vs. $(\alpha_l - \alpha_g)T_2$ for the indicated values of the coordination number z for infinite chain length (solid curve), $x = 50$ (dashed curve), and $x = 20$; (b) $zE_0(\alpha_l - \alpha_g)2k$ vs. $(\alpha_l - \alpha_g)T_2$. The usual experimental range of $(\alpha_l - \alpha_g)T_0$ is indicated on the figure.

The parameter $zE_0(\alpha_l - \alpha_g)/2k$ is shown as a function of $(\alpha_l - \alpha_g)T_2$ in Figure 1b. Owing to the way the partition function separates into terms involving n_l and zE_0 on the one hand and ϵ on the other, the relation between $zE_0(\alpha_l - \alpha_g)$, or zE_0/kT_2, and $(\alpha_l - \alpha_g)T_2$ does not depend on ϵ. For example, the same result obtains if all $z - 1$ alternative directions for a placement on the lattice have equal energy ($\epsilon = 0$), in which case the partition function is that of Flory[8] and Huggins.[9] (A similar approximation was applied by Hirai and Eyring[10a] in their version of the "hole theory" of the glassy state.) Similarly, the relation between ϵ/kT_2 and $(\alpha_l - \alpha_g)T_2$ does not depend explicitly on E_0. Consequently, the treatment of the glassy state by Gibbs and DiMarzio effectively results in two independent correlations: (1) one involving the intramolecular parameter ϵ, giving ϵ/kT_2 as a weak function of $(\alpha_l - \alpha_g)T_2$, and (2) another between $zE_0(\alpha_l - \alpha_g)$ and $(\alpha_l - \alpha_g)T_2$. If either correlation is to be useful in predicting T_2 given experimental data on $\alpha_l - \alpha_g$, one must have an independent measure of the parameters ϵ or zE_0.

It has been observed[6,7] that a correlation obtains between values of ϵ and zE_0 derived from the use of eq 1–8 on their counterpart with the Gibbs-DiMarzio partition function. The source of this correlation is evident in eq 1 or Figure 1a, where it is seen that with the lattice model, both ϵ/kT_2 and zE_0/kT_2 are functions of $(\alpha_l - \alpha_g)T_2$. Consequently, an implicit relation obtains between ϵ and zE_0 calculated with the lattice model, as shown, for example, by eq 1 or in Figure 4 of ref 7. The resultant correlation has been used[6] to connect aspects of the lattice and free volume models by computation of "universal" values of ϵ and zE_0 corresponding to the "universal" value of $(\alpha_l - \alpha_g)T_2$. We will not consider this correlation further since it has been treated in detail elsewhere.[6,7] Rather, our objective is to explore the utility of the lattice treatment per se in the estimate of T_2 from independently available data. Also in this spirit, as mentioned above, we will forego much discussion of conceptual difficulties in the use of the lattice model to treat the glassy state, albeit that some of these raise serious question on the significance of some of the parameters in the theory.[10b]

Comparison with Experiment

The ϵ Parameter. In the following discussion, we will assume that for practical purposes T_2 can be identified with the temperature T_0 in the Vogel relation[11]

$$\tau \propto \exp[1/\alpha(T - T_0)] \qquad (9)$$

for the temperature dependence of a molecular relaxation time τ (τ proportional to the viscosity) according to the free volume model[11] or the entropic model of Adam and Gibbs.[12] In terms of the familiar free volume treatment of the glassy state, T_0 is the temperature where the fractional free volume f of the hypothetical equilibrium liquid vanishes. Of course, the glass transition intervenes at $T_g > T_0$, with $T_g = T_0 + f_gB/\alpha$ according to the free volume model (here B is a parameter near unity and f_g is the value f at T_g). For many polymers, f_gB/α is in the range 50–90 K, but in some cases larger values have been reported.[11] In the following we will be concerned with T_0 rather than T_g, since the former is more logically associated with T_2 of the lattice treatments.

With this assignment, the range of $(\alpha_l - \alpha_g)T_2 \simeq (\alpha_l - \alpha_g)T_0$ observed for a wide variety of polymers is shown in Figure 1. It is evident that (for a given z and x) the reduced flex energy ϵ/kT_2 is predicted to be in a very narrow range for most polymers. For example, for $z = 4$ and $x = \infty$, $\epsilon/kT_2 = 1.42 \pm 0.10$ over the usual experimental range of $(\alpha_l - \alpha_g)T_0$ (or $\epsilon/kT_2 = 2.15 \pm 0.10$ with the partition function of Gibbs and DiMarzio). Consequently, T_2 is (nearly) proportional to ϵ and, in principle, independent information on ϵ can be used to estimate T_2. This might be a virtue of the treatment. However, if it is found necessary to treat ϵ as an arbitrary adjustable parameter to fit data, one might as well eliminate it from further consideration, as correlations involving ϵ could just as well be made directly in terms of T_2, thereby eliminating the intrusion of such a model specific parameter as ϵ.

It may be noted that in an application of the partition function, Flory calculated the fraction f_ϵ of flexed bonds,

$$f_\epsilon = Y/(1 + Y) \qquad (10)$$

necessary for the disordered state to be thermodynamically stable with respect to the ordered state with the molecules lying in a parallel array.[3] The criterion for stability of the disordered state,

$$\epsilon/kT < \ln[(z - 2)/(e - 1)] \qquad (11)$$

(for large x) requires that ϵ/kT be much less than the values of ϵ/kT_2 given in Figure 1a (for example, ϵ/kT should be less than 0.15 for $z = 4$). Similarly, calculation of the free energy with the partition function in the form used by Gibbs shows it to be positive relative to the ordered state for $(\alpha_l - \alpha_g)T_2$ in the range of interest. The indicated magnitude of the temperature interval between T_2 and the thermodynamic melting temperature of the theory is not an attractive feature of the model, since it shows that the method requires application of the partition function of Flory in a range of f for which the formulation is purposely incomplete,[3] with the effect that the number of available configurations is substantially underestimated.[3,10b]

As pointed out by Gibbs,[5] consideration of the (unperturbed) mean-square end-to-end distance $\langle L^2 \rangle$ is a natural way to attempt an estimate of ϵ. The intramolecular

Table I
Parameters Used in Comparison of T_0 with the T_2 of the Lattice Treatment[a]

polymer	T_0, K	$(\alpha_l - \alpha_g)T_0$	σ	$\partial \ln \langle L^2 \rangle / \partial \ln T$	$V_s\delta^2$ [b]	$(T_2)_{calcd}$
poly(vinyl acetate)	248	0.097	2.1		22 200	325
poly(methyl methacrylate)[c]	308	0.111	2.0	+0.17	23 100	286
poly(methyl acrylate)	215	0.062	2.0	+0.086[e]	23 400	217
polystyrene	313	0.094	2.2	+0.017	28 900	283
polybutadiene	128	0.075	1.4	+0.03	7 300	140
polyethylene	100	~0.07	1.6	−0.42	4 480	103
cis-polyisoprene	~150	0.062	1.7	+0.11	15 000	198
polyisobutylene	122	0.048	1.8	−0.03	9 100	121
poly(dimethylsiloxane)	40	0.022	1.5	+0.26	4 800	90
poly(methyl methacrylate)[c]	301	0.122	2.0		23 100	
poly(methyl methacrylate)[d]	308	0.111	2.0	+0.17	23 100	286
poly(ethyl methacrylate)	265	0.080			25 100	243
poly(*n*-butyl methacrylate)	220	0.053			28 900	225
poly(*n*-hexyl methacrylate)	178	0.046			45 500	407

[a] T_0, α_l, and α_g from ref 7 or 11 (α_l and α_g evaluated at T_g); $\partial \ln \langle L^2 \rangle / \partial \ln T$ from ref 13; and δ from ref 17. [b] V_s is the molar volume per segment. [c] Free radical PMMA. [d] Ideally attactic PMMA. [e] For poly(isopropyl methacrylate).

partition function used in the treatment of the glassy state is simplified—it corresponds to a chain with fixed bond angles and independent bond rotational angles. For this model, estimates of ϵ may be derived from either $C_\infty = \langle L^2 \rangle / nl^2$ or $\partial \ln \langle L^2 \rangle / \partial \ln T$ (here n is the number of backbone bonds of length l). Thus, the steric factor σ, equal to $\langle L^2 \rangle$ divided by $\langle L^2 \rangle_f$ for the freely rotating chain and proportional to C_∞, is expected to be a function of ϵ/kT (e.g., $\sigma^2 = (2 + y)/3y$ for a chain with a threefold symmetric potential about the preferred state, where $y = \epsilon/kT$). Further, $\partial \ln \langle L^2 \rangle / \partial \ln T$ is proportional to ϵ/kT for small ϵ/kT, with proportionality constants $-^2/_3$ and $^1/_6$ for preferred trans and gauche rotamers, respectively. Remembering the simplication of the model, one can expect that correlation of ϵ deduced from T_2 with C_∞ or $\partial \ln \langle L^2 \rangle / \partial \ln T$ will be crude. For example, it is known that one must consider interdependent rotational potentials to adequately account for the latter two parameters.[13] As expected, different estimates for ϵ are derived from data on C_∞ and $\partial \ln \langle L^2 \rangle / \partial \ln T$ for most polymers. Entries in Table I show, as is well known,[14,15] that a crude correlation obtains between σ and T_0 (e.g., between ϵ from C_∞ and T_0), with high values of T_0 tending to be associated with large σ. The correlation is too crude to be useful, and ϵ/kT_0 calculated with ϵ from σ is not even approximately constant, as is required by the lattice treatment. The preponderate positive entries for $\partial \ln \langle L^2 \rangle / \partial \ln T$ in Table I indicate a marked preference for the gauche rotamer, an erroneous conclusion that reflects the oversimplified partition function with independent bond rotational potentials.

Since neither $\langle L^2 \rangle / nl^2$ nor $\partial \ln \langle L^2 \rangle / \partial \ln T$ can be used to estimate a value of ϵ to predict T_2, the correlation $T_2 \approx 1.42\epsilon/k$ of the lattice treatment (for $z = 4$) is of little practical benefit with regard to the correlation of data on T_2 or the prediction of T_2 from data on intramolecular chain properties. Apparently, if significant at all, ϵ must be regarded as a complicated function of intra- and intermolecular interactions not amenable to independent assessment, a conclusion that has also been reached by others, e.g., see ref 6, 7, 10b, and 14.

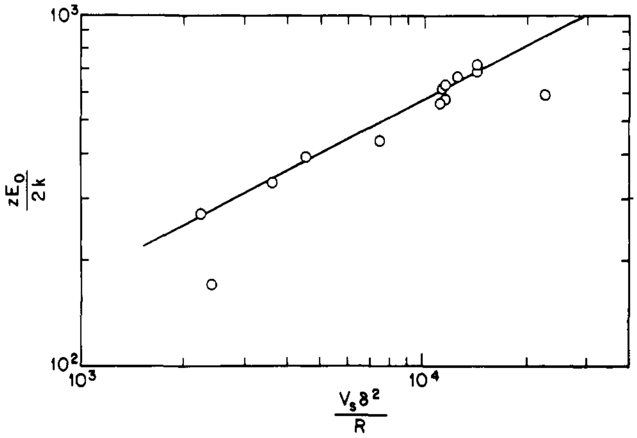

Figure 2. The intermolecular energy zE_0 as a function of the cohesive energy per mole of segments $V_s\delta^2$.

The E_0 Parameter

Turning to the correlation between $zE_0(\alpha_l - \alpha_g)$ and $(\alpha_l - \alpha_g)T_2$, one requires some estimate for zE_0 to be in a position to estimate T_2 from the results of the lattice treatment of the glassy state. As suggested by Moacanin and Simha,[7] at least a crude correlation might be anticipated between zE_0 and $V_s\delta^2$, since both parameters are in some sense determined by similar intra- and intermolecular interactions. Here, δ is the solubility parameter, V_s is the molar volume per chain segment with molar mass m_s, with a segment to be defined in some way as to be compatible with the lattice treatment involving zE_0, not necessarily equal, for example, to a single repeat unit in the chain backbone. We choose to estimate m_s from data on the unperturbed mean square radius of gyration $\langle s^2 \rangle$. Thus, we let $m_s = m_0\rho/l$, where m_0 is the molar mass per repeat unit with contour length l, and ρ is the persistence length. The latter is calculated as $\rho = 3(m_0/l)(\langle s^2 \rangle / M)$. For the most part, the number m_s/m_0 of monomer units per segment calculated this way lies in the range 2–3.5. The correlation between zE_0, determined with Figure 1a and the $(\alpha_l - \alpha_g)T_0$ in Table I, and $V_s\delta^2$, shown in Figure 2, is fitted by the relation

$$zE_0/k = 11.56(V_s\delta^2/R)^{1/2} \text{ (K)} \tag{12}$$

with δ^2 in conventional units (calories/milliliter), V_s in milliliters (moles of segment)$^{-1}$, and R the gas constant. The data for poly(dimethylsiloxane) and poly(n-hexyl methacrylate) show the largest deviation from eq 12. (The correlation is more satisfactory than would be obtained with the use of the molar volume per repeat unit instead of V_s.) The primary source of uncertainty in the data listed is the value for $\alpha_l - \alpha_g$, which enters into the calculation in an important way but is not always precisely known. In view of the manner in which E_0/kT is introduced in a sort of van Laar heat of mixing term in the partition function, the proportionality of zE_0 to the square root of

$V_s\delta^2$ is surprising. However, it is interesting to note that a similar correlation obtains between the critical surface tension γ_c and δ. Following Hildebrand and Scott,[18] one can consider the relation between the free energy of surface formation per mole, here taken to be proportional to $\gamma_c V_s^{2/3}$, and the cohesive energy per mole, $V_s\delta^2$. Whereas for small molecules it appears that $\gamma_c V^{2/3}$ is nearly proportional to $V\delta^2$, the data on polymers are fitted much better by $\gamma_c V_s^{2/3}$ proportional to $(V_s\delta^2)^{0.65}$—the correlation between γ_c and δ was noted previously by Gardon.[19] Thus, it appears that zE_0 is nearly proportional to a surface free energy $\gamma_c V_s^{2/3}$ according to the analysis given here. This identification is in the spirit of a free volume model used by Bueche[20] and, later, Litt[21] in which the average free volume is calculated with a Boltzman factor involving the surface energy.

The agreement between T_2 calculated with data on $(\alpha_l - \alpha_g)$ and $V_s\delta^2$ by using eq 11 and Figure 1b and experimental values of T_0 is not uniform. Calculated values of T_2 entered in Table I are generally within 20 K of T_0, but occasional discrepancies may be much larger, as with poly(vinyl acetate) and poly(n-hexyl methacrylate). The error probably reflects uncertainty in $\alpha_l - \alpha_g$ and the overall crudeness of the correlation between zE_0 and $V_s\delta^2$, as well as the limitations of the lattice model leading to the correlation between $zE_0(\alpha_l - \alpha_g)$ and $(\alpha_l - \alpha_g)T_2$.

Finally, it should be noted that for convenience, values of $\alpha_l - \alpha_g$ given in Table I are evaluated at T_g rather than T_0. In general, α_l will depend on temperature and should be evaluated at T_0 for our purpose. Variation of α_g over the range T_g to T_0 is probably less serious. For some materials, it appears that the density ρ is nearly linear in temperature over wide temperature intervals.[22] For example, the reduced equation of state given by Simha and Weil[23] exhibits such behavior in the range of interest here. If ρ is linear in T, then the $\alpha_l - \alpha_g$ evaluated at T_0 can be expressed in terms of $\alpha_l - \alpha_g$ evaluated at T_g by the relation

$$(\alpha_l - \alpha_g)_{T_0} = (\alpha_l - \alpha_g)_{T_g}\{1 + [\alpha_l/(\alpha_l - \alpha_g)]_{T_g}{}^2(\alpha_l - \alpha_g)_{T_g}(T_g - T_0)\}^{-1} \quad (13)$$

This equation predicts that $\alpha_l - \alpha_g$ at T_0 is about 10% smaller than $\alpha_l - \alpha_g$ at T_g for the polymers entered in Table I, except for poly(dimethylsiloxane) and poly(n-hexyl methacrylate), for which the decreases are about 40% and 17%, respectively. (Typically, $\alpha_l/(\alpha_l - \alpha_g)$ is about 2, and $(\alpha_l - \alpha_g)(T_g - T_0)$ is about 0.025, the so-called "universal" value used in the well-known WLF relation.[11,14,15]) Since use of the modified values of $\alpha_l - \alpha_g$ would have a very slight effect on the correlation shown in Figure 2, we have chosen to use the more readily available parameter evaluated at T_g.

Conclusion

As remarked in the introduction, the lattice treatment of the glassy state put forward by Gibbs, with results summarized in Figure 1 (for undiluted polymers), includes a number of simplifications that raise questions concerning the fundamental basis of the theory. These several stipulations aside, our limited objective has been to investigate the utility of the results in Figure 1 for purposes of predicting T_2 (assumed to be equivalent with T_0), given independent assessment of α_l, α_g, zE_0, and ϵ. We have found that the calculated dependence of T_2 on the flex energy ϵ cannot be used with intramolecular estimates of ϵ to predict T_0. Others have reached the same conclusion if T_2 is approximated by T_g.[6,7] Although this failure is understandable in view of the simplifying assumptions made in the theory, it does, none-the-less, represent a limitation in the application of the results to estimate $T_0 \simeq T_2$ and illustrates one effect of some of the approximations introduced in the theory. Somewhat to our surprise, a correlation has been found between the hole interaction energy zE_0 and the free energy of surface formation $\gamma_c V_s^{2/3}$, which in turn is related to the cohesive energy density. In this correlation, zE_0 is evaluated from that part of the lattice theory in which the flex energy does not enter in any way. It may be of interest to investigate possible support for this correlation within the frame of the simplified "Flory–Huggins type" partition function, although many of the criticisms mentioned above would remain.

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