(8) C. C. Hsu and J. M. Prausnitz, *Macromolecules*, **7**, 320 (1974).
(9) A. Robard, unpublished calculation.
(10) M. Bank, J. Leffingwell, and C. Thies, *Macromolecules*, **4**, 43 (1971).
(11) C. S. Su and D. Patterson, *Macromolecules*, **10**, 708 (1977).
(12) A. Robard, D. Patterson, and G. Delmas, *Macromolecules*, **10**, 706 (1977).
(13) D. Patterson, H. P. Schreiber, Y. B. Tewari, and J. E. Guillet, *Macromolecules*, **4**, 356 (1971).
(14) J. S. Rowlinson, "Liquids and Liquid Mixtures", 2nd ed, Butterworths, London, 196, p 166.
(15) D. D. Deshpande and S. L. Oswal, *J. Chem. Soc., Faraday Trans. 1*, **68**, 1059 (1972); C. Booth and C. J. Devey, *Polymer*, **12**, 309 320 (1968).

Configurational Thermodynamics of the Liquid and Glassy Polymeric States

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ABSTRACT: The basis, assumptions, and essential results of a molecular theory and comparisons with experiment are reviewed. An effective principle of corresponding states obtains and correlations between the scaling parameters, exceptions, and implications are discussed. An important quantity is the hole or unoccupied volume fraction h. In the equilibrium liquid its volume and temperature dependence results from the minimization of the configurational Hemlholtz free energy. The relation between liquid–glass transition lines for variable and constant formation histories is obtained in the form of a generalized Ehrenfest equation in terms of h. PVT studies clearly indicate the continuing significance of structural contributions to the thermodynamic functions far below T_g, as expressed by variations of the h function. The entropy surface of a given glass, however, is not uniquely determined by this function. It is proposed to accomodate this feature in the frame of the present molecular theory through c, the number of effectively external degrees of freedom. While c remains practically constant in the liquid range, it should decrease with decreasing temperature in the glass, in contrast to h, which decreases more slowly. Finally, future directions for the liquid and the glass under quasiequilibrium conditions are suggested.

The many-body problem represented by the theoretical description of a disordered system, such as the liquid state at equilibrium, has remained a classical problem since van der Waals' times. Almost all efforts have been concentrated on "simple" liquids, i.e., those with spherically symmetrical force fields. Two types of analytical approaches can be distinguished. One starts out from rigorous statistical mechanical relationships and then by necessity continues by introducing well-defined approximations. In the second the point of departure is an intuitively more or less appealing model of the liquid state which then can be evaluated comparatively easily.

It is a theory of the second kind which is the primary concern here, because it has been extended to chain molecular fluids and when properly modified is quantitatively successful. We refer to the theory of Lennard-Jones and Devonshire (LJD). Its basis, results, and extensions are reviewed in several textbooks of statistical mechanics and it suffices here to recall its basic feature. The fluctuating field exerted by the surrounding constituents on a given particle is replaced by an average field which is defined by placing the former on a lattice and permitting the central molecule to move in the cell formed by its neighbors under a prescribed pair potential. In the simplest formulation correlations between particles entrapped in adjacent cells are neglected.

A pioneering extension of this model to chain molecular liquids was presented some time ago by Prigogine and his colleagues,[2] who dealt not only with the one-component systems of interest here but also developed a basic approach to mixtures. In spite of the well-known deficiencies of the cell theory, a solid-like theory, when applied to rare gas and similar liquids, it has been more successful for oligomer fluids[3] and amorphous polymers.[4,5] Moreover it became the starting point for semiempirical extensions.[6] The introduction of additional disorder by vacancy sites[7] improves the situation considerably in respect to the configurational thermodynamic functions. The presence of a hole or free volume fraction as a function minimizing the configurational free energy leads quite naturally to the consideration of liquid–glass boundaries, the glassy state as a partial equilibrium system, and the connection between the liquid and its glasses, generated in a specified manner.

We take this occasion first to recapitulate and to comment on the assumptions of the theory and to point to conclusions derived from applications to amorphous polymers and polymer melts, including some recent data. Second we consider implications for the glassy state.

(I) The Liquid State

(A) Assumptions. (1) The linear chain is subdivided into segments, each moving in the field of its intermolecular neighbors. The dissymmetry due to the intramolecular neighbors is disregarded. The basic intersegmental pair potential is taken to be of the 6–12 form and the resulting cell potential is simplified at ordinary temperatures to a square well. At low temperatures, in practice the cryogenic range for polymer glasses, an expansion of the LJD cell potential, yields a quasiharmonic expression, with the force constant an explicit function of volume.

(2) In addition to the geometric parameter, the number s of segments per chain, a dynamic parameter arises in the following manner: In the evaluation of the configurational partition function, only those modes of motion are to be included which are determined or modified by intermolecular interactions, in other words, external degrees of freedom. Their identification is clear-cut in the simple structures which have been the usual testing ground for theories of the liquid state. There, the number $3c$ of pertinent degrees of freedom equals 3 or 6 for a spherically symmetrical and a rigid (no internal rotations) asymmetric structure, respectively. Another extreme immediately identified is the ideally flexible chain, where the energy barriers for internal bond rotation are low in comparison with intermolecular effects. If furthermore no flexible (in this sense) side chains are present, $3c = s - 3 + 6$

= $s + 3$, and as s increases, the characteristic flexibility ratio $3c/s$ remains finite. Thus in all instances cited a clean separation between "soft" and "hard" modes exists. In a real flexible chain lacking either of the above attributes, it is still possible to identify groups of internal modes, such as bond stretching and bending. However, the bond rotations in the backbone and motions in flexible side chains may not belong to this class but may be modified in the transition to the dense state. The requisite superposition of intra- and intermolecular contributions to the partition function is straightforward in principle in a normal mode decomposition, which however is inappropriate in the liquid range. No treatment has been offered so far.[8] Instead we have the original proposal of Prigogine et al.[2] who clearly recognized the problem stands. These authors decouple hard and soft modes by *assuming* the existence of a number $3c$ of external modes, which cannot be specified a priori. Moreover, c is to remain constant with changing volume and temperature. The flexibility ratio c/s enters the definition of the scaling temperature and thus is derivable from experiment (see below).

(3) As mentioned previously, the cell theory in the Prigogine formulation is quantitatively superior to what one should anticipate from the results for simple liquids. Previous empirical isothermal density–molecular weight relationships for n-paraffins[3a] and other hydrocarbon structures[3b,c] are derived, volume–temperature curves for oligomers and polymers in the low-temperature range are in accord with experiment,[4,5a] and pressure effects can be accounted for semiempirically.[5b,6] Such successes are primarily due, we believe, to the comparatively low actual or reduced temperatures (see below) involved.

Yet, these results are limited to the lower ranges of the reduced temperature scale. A noticeable improvement ensues when the disorder in the model is enhanced by the introduction of vacancies or holes in the quasilattice, while retaining the mathematical advantages of a lattice model.[7] The partition function contains an additional factor corresponding to the entropy of mixing of a specified number of holes and chains. It is evaluated by assuming random mixing of vacant and occupied sites of equal size and applying the expressions of Flory and of Huggins in their simplest form. A characteristic feature of cell theories is the appearance of a statistical mechanical free volume, not to be confused with the unoccupied volume introduced in empirical descriptions. Here a further assumption is made, namely a linear averaging of gas and solid-like contributions over the fraction h of empty sites. There is a similarity here to Eyring's theory of significant structures.[9] More satisfactory results are obtained when this averaging is performed over modes or lengths then over volume[7] and it has been adopted in all subsequent applications. Finally, the lattice energy term, corresponding to a localization of all segments on their sites, now also depends on h.

(B) Comments. The representation of segments as 6–12 point centers at the distances involved may be questioned and replaced in a refined theory by an atom to atom summation, as employed in the theory of Chandler and his colleagues[10] for liquids of asymmetric rigid molecules. Alternative intersegmental potential functions for polymer liquids have never been used, for one reason because the requisite lattice summations and cell potentials are not available. We believe this should not be significant, as long as a reasonable repulsive term is retained. The numerical values of the scaling parameters to be discussed subsequently and possibly the dependence of h on V and T may be altered, but the configurational energy, for example, remains unchanged. This conjecture is based on results discussed below.

The square well approximation seems reasonable. Alternative forms approximating the LJD cell potential have been used,[2] with no significant differences in the end results. Actually the square well extends the validity of the cell theory to higher temperatures than an alternative form.[4,5a] The complete LJD expression would produce a dependence of the free volume on volume and temperature, where the square well in the absence of vacancies produces a dependence on V only. These observations and the increased computational effort required do not encourage the introduction of the rigorous LJD potential. At low temperatures an expansion of this potential is appropriate for the discussion of low-temperature glasses.[11] More recently it has been shown that the equation of state of polymer crystals can also be successfully described, when the expansion is carried to one additional term.[12]

The free-volume approximation can only be vindicated by alternative analytical approaches or computer simulation. We can only say that it yields a physically reasonable behavior of the hole function, besides of course providing an equation of state in close agreement with experiment.

Comments on the c factor will be postponed until the discussion of results.

(C) Results. The thermodynamic functions are expressable in reduced variables in terms of a scaling temperature T^*, volume V^*, and pressure P^*. For large s, these quantities are defined as follows:

$$T^* = (s/c)(z-2)\epsilon^*/k$$
$$P^* = s(z-2)\epsilon^*/(sv^*) \qquad (1)$$

Here v^* and ϵ^* are defined by the segmental pair potential as the repulsive or hard-core volume and the potential minimum, respectively, and z is the coordination number of the quasilattice, set equal to 12 in the numerical evaluations, with $z - 2$ the average number of nonbonded nearest neighbors. The numerical values of these parameters are known by now for a large number of systems. They are obtained by numerical or graphical superposition of theoretical and experimental isotherms and isobars with no further adjustments permissible in calculating compressional energies and entropies. We note in eq 1 that the flexibility ratio c/s is absorbed in the scaling temperature. In the cell theory and with the square well approximation, it does not appear explicitly. The introduction of holes however changes the situation. The hole fraction h is derived as a function of the reduced variables $\tilde{V}$ and $\tilde{T}$ by a minimization of the Helmholtz free energy. The resulting conditional equation involves explicitly c/s, a not unexpected result. It should be possible to obtain consistent values for different oligomers and polymers by solving the equilibrium condition for a series of c/s values and obtaining the best fit to experimental data. This turns out to be impossible because the resulting theoretical isotherms and isobars are superimposable[7] and hence they will superimpose equally on the experimental curves. No independent method of arriving at a c value, except for small molecules and even these values are questionable, seems to be available. Thus we continue with an additional assumption by the assignment $3c/s = 1$. This value would correspond to an ideally flexible s-mer without soft side chain motions, which now replaces the real chain consisting of n repeat units. This serves then to define the segment. In a simple structure, it will encompass more units, for example, in polymethylene about 2.5CH_2 units, whereas in n-butyl methacrylate, the segmental molecular weight turns out to be only one-half the averaged molecular weight per back bone unit.[13] Thus the volume of the segment will be a compromise between size and fine structure of the repeat unit.

We can dispense with an explicit display of the equation of state and determining equation for h and want to point only to some specific features. All thermodynamic functions and the pressure equation can be cast in the reduced form

$$\tilde{Q} = \Phi[\tilde{V},\tilde{T}] \qquad (2)$$

with the condition

$$(\partial\tilde{F}/\partial h)_{\tilde{V},\tilde{T}} = 0 \qquad (3)$$

where F is the Helmholtz free energy. The transcendental eq 3 requires a numerical solution, to be substituted in eq 2. This presents no particular problem. However, for practical applications it is convenient to have explicit expressions. At atmospheric pressure, the theoretical equation of state can be in excellent approximation represented by the following interpolation formula:[14]

$$\ln\tilde{V} = -0.1034 + 23.835\tilde{T}^{3/2};\ 1.65 < \tilde{T} \times 10^2 < 7.03 \qquad (4)$$

or

$$\ln\tilde{V} = -0.1034 + (2/3)\alpha T$$

$$\tilde{\alpha} = (1/V)(\partial V/\partial\tilde{T})_P = 35.735\tilde{T}^{1/2}$$

Equation 4 accurately represents the reduced curves derived earlier from experimental data.[4] It also provides a more stringent test of the theory by means of thermal expansion measurements. Theoretical deficiencies when not excessive can be remedied by empirical adjustments of scaling parameters with changing temperature and volume. Such a device was first employed by us in applying the Prigogine theory to *n*-paraffins.[3a] Detailed measurements,[15a] literature data, and analyses[15b] on several structurally diverse organic polymers show the following results: Over a range of 100 °C, the parameter V^* changes maximally and minimally by 2 and 0.4%, respectively, whereas variations in T^* are between 9 and 2%. Although experimental errors may in some instances play a role, the changes are systematic. Both V^* and T^* increase with temperature. Formally this would imply a slight decrease of c, see eq 1, hence with our assumptions of s as well, and thus an enlargement of the segmental volume v^*, all this being physically reasonable. The thermal expansivities are still quite accurately expressed by the theory, with deviations never reaching 10%. However, the temperature coefficients $d\alpha/dT$ are smaller than is predicted by the square-root dependence, eq 4. In other words, the differences between theory and experiment become significant in the third derivative of the partition function. By pursuing some ideas of Bueche[16] based on an entirely different approach, Litt arrives at an expression quite similar to eq 4,[17] namely

$$\tilde{V} = [1 - (2/3)\alpha T]^{-1};\ (2/3)\alpha T = \tilde{T}^{3/2}/(1 + \tilde{T}^{3/2}) \qquad (4')$$

The scale factors are differently defined, but eq 4 and 4′ are identical up to terms $0(\alpha T)$. Thereafter eq 4′ yields a slower increase of α with T then 4.

Next it is instructive to examine the hole function h, obtained by solution of eq 3. It turns out that the product $(1 - h)\tilde{V}$, which represents the volume occupied by a cell, remains approximately constant over a wide range of temperature and volume.[7,15b] This is particularly so in the range of reduced temperatures in eq 4 appropriate to organic polymers and oligomers at atmospheric pressure. Thus we can write for the unoccupied volume fraction

$$f \equiv h \simeq 1 - \tilde{V}_0/\tilde{V} = 1 - V_0/V \qquad (5)$$

Here $\tilde{V}_0$ changes from 0.947 to 0.967 as $\tilde{T}$ increases by a factor of 4. Thus V_0 corresponds to a "vibration" volume. It is noteworthy that this simple result emerges from the detailed considerations described earlier. The theory, of course, goes beyond that by providing an explicit expression for the temperature coefficient

$$1/f\ df/d\tilde{T} \simeq [(1 - h)/h]\tilde{\alpha} \qquad (5a)$$

The result (eq 5) leads to an important conclusion regarding the configurational internal energy U. The following expression is derived:[7]

$$2\tilde{U} = 2U/(P^*V^*) = y(y\tilde{V})^{-2}[2.409 - 1.011(y\tilde{V})^{-2}] \qquad (6)$$

with $y = 1 - h$. In view of eq 5, this reduces approximately to the product of a slowly varying function of volume and y. Hence U becomes approximately proportional to $1/V$, that is the van der Waals form derived from an entirely different model. Thus it is seen again that the introduction of vacancies in the lattice model with the assumptions discussed earlier modifies the results of the cell theory considerably. It will also be recalled that a van der Waals term is introduced in an ad hoc manner in some other approaches to the equation of state of dense fluids. This V^{-1} dependence is however only approximate. Indeed, considering the internal pressure $P_i = (\partial U/\partial V)_T$, the product $\tilde{P}_i\tilde{V}^{-2}$ is not constant but proportional to a fractional power of $\tilde{V}$,[6] which varies approximately between ⅔ and 0.99, as derived from experimental data on oligomers and polymers.[18]

No detailed examinations of P^* variations, as indicated by volume–temperature measurements at elevated pressures, have been undertaken, but we can quote two results. For poly(vinyl acetate), up to 800 bar, a standard deviation of 1.7% from the average value of P^* results. More recently Zoller has studied the equation of state of poly(tetrafluoroethylene) in a pressure and temperature range of about 2 kbar and up to 372 °C, corresponding to a reduced temperature of 8.16×10^{-2},[20] higher than was reached in previous studies. A standard deviation of 4% is observed. These results, investigations of further systems,[15a,21,22] and literature show good agreement between theory and experiment up to moderate pressures ≤ 2 kbar. No data at higher pressures have been reported, which would require higher temperatures with an enhanced posibility of thermal degradation. Another limitation is the reduction in the liquid range of pressures at low temperatures.

We note finally that highly accurate polynomial solutions of the equilibrium condition, eq 3, have been derived recently,[23] albeit for a limited range, viz., $2.5 \leq \tilde{T} \times 10^2 \leq 4.0$; $0 < \tilde{P} \leq 0.100$. Expressions are given as functions of $\tilde{V}$ and $\tilde{T}$ and also of $\tilde{P}$ and $\tilde{T}$. These are then substituted into the explicit form of eq 2 to yield the equation of state. Similar expansions are also presented for the configurational reduced energy and entropy, convenient for the calculation of corresponding heat capacity contributions.

Before concluding this section a brief comment on the empirical Tait equation of state, $1 - V/V_0 = C\ln(1 + P/B)$, is in order. As has been shown repeatedly, it serves well in the manipulation of experimental P–V–T data, in terms of a single adjustable temperature function $B(T)$, which is approximated by the exponential expression

$$B(T) = B_0\exp(-B_1T)$$

while a universal value can be assigned to the second dimensionless quantity C. The cell theory shows C to be a very slowly varying function of temperature.[24] No consistent analysis in terms of the hole theory has been given. If the constancy of C is accepted as an empirical result, the theory yields just the temperature dependence obtained experimentally.[14,18] In reduced form the equation is:

$$\tilde{B} = 0.9549\exp(-49.22\tilde{T})$$

This permits at least an estimation of high pressure from low pressure densities.

(D) The Scaling Parameters. The work referenced has produced the scaling quantities defined by eq 1 for a sufficiently large number of systems, so that comparisons could be undertaken, and with some exceptions rationalized in terms of structural characteristics. An extensive tabulation of these and derived parameters is given in ref 13 and will not be re-

Table I
Characteristic Parameters

Material	T^*, K	V^*, cm^3 g^{-1}	P^*, bar	M_0/M_{rep}
Poly(dimethylsiloxane)[25]	7893	0.9602	5061	0.61
Poly(tetrafluoroethylene)[20]	7906	0.424	6960	1.48
Selenium[26]	14180	0.2414	17050	1.21

produced here. It results in the following correlation between the scaling entropy factor $S^* = P^*V^*/T^*$ and T^*:

$$\ln S^* = 1.319 - (3/2.01) \times 10^{-4}T^* \tag{7}$$

This equation represents the results for n paraffins between C_7 and C_{40} well. In the high molecular weight range, the limits are: $0.71 < V^* < 1.17$; $0.92 < 10^{-4}T^* < 1.3$; $6.7 < 10^{-3}P^* < 10.4$.

The practical utility of this correlation for estimating P^* in the absence of pressure data is obvious. It implies that a large attractive energy ϵ^* and thus temperature T^*, with the corresponding low $\tilde{T}$, results in a low entropy. Decomposition of S^* into its constituent factors yields

$$S^*/R = (c/s)/M_0$$

where S^* represents an entropy per unit mass and M_0 is the segmental molecular weight. The appearance of the factor 3/2 in eq 7 is remarkable and indicates a 2/3 dependence of T^* and ϵ^* (see eq 1) on M_0. This further suggests a correlation with the surface of the segment. The result is of the form

$$10^{-4}T^* = \ln (M_0V^*/A)^x \tag{7a}$$

where $A = 9.3$ or 7.4 and $x = 2.1/3$ or 2.2/3. The n paraffins, polyethylenes, and hevea rubber require the first, whereas the remainder are approximated by the second set of values.

From eq 7 there follows:

$$c/n = 4.50 \times 10^{-2}M_{\mathrm{rep}} \times \exp[-4.478 \times 10^{-3}\epsilon^*/k] \tag{7b}$$

with

$$\epsilon^* = \epsilon^*_{\mathrm{rep}}(n/s)$$

where M_{rep} and $\epsilon^*_{\mathrm{rep}}$ represent the molecular weight and maximum attractive energy for each of the n repeat units. Equation 7b indicates how the number c of effective degrees of freedom per repeat unit decreases as n/s and thus the size of the segment increases. Since a fixed ratio c/s has been imposed, a relation between this size and the characteristic energy $\epsilon^*_{\mathrm{rep}}$ for a specified M_{rep} obtains, namely:

$$n/s = (7.4/M_{\mathrm{rep}}) \exp[4.478 \times 10^{-3}(\epsilon^*_{\mathrm{rep}}/k)(n/s)] \tag{7c}$$

As the cohesive energy increases, the ratio n/s decreases, and the size of the segment required for a specified number of external degrees of freedom is reduced. Equation 7c represents in this manner the influence of the intermolecular potential on the parameter c in the expected direction. The effect is pronounced. For values of $\epsilon^*_{\mathrm{rep}}/k$ of the order of 10^2 to 10^3 (see Table I in ref 13), an increase of the energy by 50% reduces n/s by a factor of 2 or more for values of M_{rep} of the order of 10^2 to 10.

Three systems not included in Table I of ref 13 are shown in Table I. All three have parameter values outside the range for which eq 7 was established and show significant departures, with S^* being considerably lower than predicted. For the siloxane P^* is small (small ϵ^*) and, consistently, T^* is also too small compared with the values for carbon backbone polymers in ref 13. Teflon has a small V^* and T^* is also comparatively small. As one might expect, Se stands apart in respect to all three quantities. A strong attraction results in a very large T^* and P^*, and V^* is small. It is not surprising that the simple repeat unit (ring structures have been disregarded in the analysis) does not satisfy the 2/3-relationship, but neither does the siloxane. Teflon on the other hand obeys the same correlation with segmental volume as polyethylene.

This concludes the discussion of the liquid state. Heat capacities will be considered in the next section.

(II) The Glassy State

(A) General Considerations. The question arises whether a connection can be established between the melt and the glass in terms of the configurational functions computed for the liquid. Which features of the equilibrium description can be retained in the discussion of a quasiequilibrium state of the glass? On narrower grounds one may inquire whether the conventional (low frequency) glass transition temperature T_g can be characterized by a universal value of one or the other of the parameters appearing in the theory. This can be answered immediately. First, T_g is not a corresponding temperature; $\tilde{T}_g$ does not assume a universal value, but decreases with decreasing T_g.[15b] For plastic materials $\tilde{T}_g$ values cluster around 3 to 3.5×10^{-2}, whereas the few data available for rubbery polymers indicate values as low as 2×10^{-2}. On such grounds incidentally, one should anticipate a glass temperature of about 200 K for polyethylene ($T^* \simeq 10^4$) which is in accord with values suggested by dilatometric and other measurements. Another question concerns the unoccupied volume fraction h at T_g. Again there is no constancy, but a trend. With increasing $\tilde{T}_g$, h_g increases at atmospheric pressure from about 1 to 9×10^{-2}.[15b] That is, a high T_g implies a relatively large free volume necessary to reach the liquid state.

Reverting to the principal question raised at the beginning, we must obviously omit to begin with at least relaxational processes. That is, the pertinent experimentation must be carried out rapidly compared with the characteristic relaxation rates of the system. In practice this implies that the neighborhood of the transition region is to be avoided. The existence and properties of a glass transition can only be derived by kinetic arguments. It will be accepted here as a macroscopic datum. The nonequilibrium character of the system is then manifested by memory effects or a dependence on the previous thermal history.[19,27,28] An extensive quantity Q may be written in the following functional form:

$$Q = Q(P,T;P',r) \text{ or } Q = Q(P,T;T',\rho) \tag{8}$$

where r is the rate at which the liquid is cooled into the glassy range under a pressure P', and T' and ρ represent a formation temperature and pressurization rate, respectively. We will be dealing here with the former manner of experimentation only. In the usual pressure experiments aimed at the pressure coefficient of T_g, the liquid is cooled at a fixed r, but under a series of pressures P', which generate a series of different glasses. On the other hand, the intersection of the liquid P–V–T surface with the corresponding surface of a glass obtained at a given r and P' yields a second pressure coefficient $dT_g^\dagger/dP$ and transition line, where $T_g^\dagger$ is a function of P, r, and P' and, in accord with eq 8, characterizes a single glass.

(B) Assumptions and Results. The existence of a quasiequilibrium state will be built into the frame of the liquid state theory by removing the equilibrium condition, eq 3, but *retaining* the mathematical form of eq 2. Thus we can write the following two general expressions:

$$-P = (\partial F/\partial V)_{T,h} + (\partial F/\partial h)_{V,T}\,(\partial h/\partial V)_T$$
$$-S = (\partial F/\partial T)_{V,h} + (\partial F/\partial h)_{V,T}\,(\partial h/\partial T)_V \qquad (9)$$

At equilibirum the second term on the right-hand side vanishes, and in the surviving term h varies with V and T in accord with eq 3. Owing to our assumption, the function $h(V,T)$ solely is to distinguish between melt and glass. We can then interpret the derivatives at fixed h as lattice contributions, whereas the remaining terms denote contributions due to the variations of the structure in the glass with varying V and T.

In the light of the well-known concepts and results of order parameter descriptions,[27] it is suggestive to assume $h = h(T = T_g) =$ constant for $T < T_g$, in eq 9. Somcynsky first demonstrated that this seriously underestimates experimental thermal expansivities at T_g, with the discrepancy being reduced, as T_g decreases.[29] Thus, the free volume fraction h is not constant in the glass. All subsequent investigations of the equation of state and the compressional energy and entropy are in accord with and amplify this result.[15b,19,23,26,30]

The equation for the transition line $T_g(P)$ can be written as follows:

$$\mathrm{d}T_g/\mathrm{d}P = (\partial T/\partial P)_h + (\partial T/\partial h)_P\,\mathrm{d}h/\mathrm{d}P \qquad (10)$$

where the relation between T, P, and h is obtained from eq 2 and 3. The last derivative is to be taken along the transition line. Introducing $T_g{}^\dagger$, eq 10 can be transformed to:[23,31]

$$\mathrm{d}T_g/\mathrm{d}P = \mathrm{d}T_g{}^\dagger/\mathrm{d}P(F_T/F_P) + (\partial T/\partial h)_P\,\mathrm{d}h/\mathrm{d}P \quad (10a)$$

where the so-called freezing fractions, F_T and F_P, are defined as:

$$F_{X_i} = 1 - (\partial h/\partial X_i)_{X_{k,g}}/(\partial h/\partial X_i)_{X_{k,l}} \quad (i \neq k)$$

X_i and X_k denote P or T, and g and l refer to the glass and liquid, respectively, at T_g, with the F_l computed from theory. $1 - F_{X_i}$ therefore may be regarded as a measure of the residual liquid structure in the glass. Equation 10a has been tested for polystyrene, poly(*o*-methylstyrene),[30] selenium,[26] and in particular poly(vinyl acetate),[19,23] where two glasses, formed at atmospheric pressure and 800 bar, respectively, were examined. Moreover, F_T at atmospheric pressure is known for a number of systems.[15b] In accord with the behavior of h in the glass mentioned earlier, F_T is observed to approach unity for low T_g and to decrease to values as low as 0.5 for a polycarbonate. We refer for detailed discussion to the original references and mention only that F_P and F_T are nearly equal to each other in Se[26] and in poly(vinyl acetate) for the glass of fixed formation history.[23] Since the reduced glass temperatures are about 0.02 and 0.03, h is approximately constant and $F \simeq 1$ only in Se. Thus it appears that the constant formation line $T_g{}^\dagger$ can be identified with the locus of all points in the T–P plane which satisfy the condition $h =$ constant and hence can be predicted by a single point determination. We remark that the equality of F_P and F_T implies the equality of the derivative $(\partial P/\partial T)_h$ for the melt and constant formation glass at the transition, i.e., an equality of the lattice contributions to the internal pressure. This in turn follows from the continuity of T, P, and h along the $T_g{}^\dagger$ transition line.[25]

Experiment indicates that h does in general not represent a frozen ordering parameter. This, of course, does not negate the existence of such parameters. It does however negate the concept of the glass as a system frozen to such an extent that only lattice type contributions to the configurational thermodynamic quantities survive. We recapitulate here briefly two arguments against such a concept, one arising from theory and the other from experiment. In addition to the evidence just cited, it has been demonstrated that lattice contributions, as calculated from cell theory, accurately account for the thermal expansivity α of several organic polymers in the range of about 10 to 50 or 70 K, depending on the system.[11] That is, h is *effectively* frozen at extremely low temperatures. Above this range, this assumption results in values which are considerably smaller than is observed. It is pertinent to recall in this connection the relation $\alpha V = -(\partial S/\partial P)_T$. This result then is consistent with a *gradually* decreasing configurational entropy. All polymers studied in the cryogenic range had elevated glass temperatures and detailed studies of rubbers below T_g are of interest, where the extent of freeze-in is high to begin with. The anticipated change in the temperature coefficient of h at the β relaxation is also observed.[15b,21b] The other argument arises simply from the fact that thermal expansivities display the sub-glass relaxations seen in dynamic data.[32]

Equations 10a and 10 have been used so far to characterize the extent of liquid-like character in the glass in terms of the two F functions and to establish a generalized Ehrenfest relation involving molecular theory. As shown by McKinney[31] they provide furthermore an estimate of memory effects arising from the functional dependence symbolized by eq 8. As a quantitative measure of the well-known densification effect, consider the coefficient

$$\kappa' = -(1/V)\,(\partial V/\partial P')_{P,T}$$

formally obtained by interchange of P and P' in the definition of the isothermal compressibility for a glass generated by cooling at a specified rate under pressure P'. In the many systems with differing T_g's examined so far,[25] κ' is positive. A direct measurement of κ' in an organic polymer was first made by Shishkin.[33] On the other hand, expressions relating κ' to other quantities can be derived and evaluated either solely by experiment or in combination with theory. On evaluating the volume changes in passing from the liquid into the glassy range under two formation pressures, the following equation is obtained:[31]

$$\kappa' = \Delta\alpha(\Delta\kappa/\Delta\alpha - \mathrm{d}T_g/\mathrm{d}P) \qquad (11)$$

where the symbol Δ indicates changes at the transition and eq 11, a linear approximation, strictly applies to the neighborhood of T_g and for moderate pressures. An estimate of the errors involved for the case of poly(vinyl acetate) shows eq 11 to be a good approximation even at lower temperatures. The repeatedly observed positive values of the parentheses are in accord with a positive densification. Various experimental procedures for the determination of the terms in eq 11 have been compared with each other.[25] On the other hand, theory may be introduced by using the well-known identity between $\Delta\kappa/\Delta\alpha$ and $\mathrm{d}T_g{}^\dagger/\mathrm{d}P$, as discussed for example by Goldstein.[27] This derivative in turn can be computed as $(\partial T/\partial P)_h$, when $F_P \simeq F_T$, see eq 10 and 10a. The agreement between the results of this calculation and measurement is quite satisfactory,[25] considering the limited accord between experimental results from different sources for presumably the same polymer. The various procedures lead to κ' values in the range of 2 for rubbery polymers to more than 10 Mbar^{-1}.

In the foregoing eq 2 has been combined with P–V–T experimentation for constant formation glasses, rather than with the condition for thermodynamic equilibrium, eq 3, to obtain the h function. Since *by assumption* this completely defines the system, we are in a position to compute not only the variation of the configurational energy and entropy with pressure but also isobaric and isochoric temperature coefficients or heat capacities. For the equilibrium system one obtains in this manner the contributions of the effectively external degrees of freedom to the total heat capacity. For three vinyl polymers C_P(conf) is found to range between 12 to 19% of C_P.[23] A separation of configurational contributions can be accomplished experimentally by measuring the pressure coefficient of C_P or the temperature coefficient of α. Accurate expansivity data are available, but no such evaluation has been made. The comparison with theory would be inconclusive in this instance due to the quantitative deficiencies mentioned earlier.

For the glass it is important to investigate the changes ΔC_P and ΔC_V occurring at the transition. The appropriate measurements for the poly(vinyl acetate) glass formed and examined at atmospheric pressure have been evaluated recently.[23] The computed configurational contribution to ΔC_P is 47% and only 13% to ΔC_V. A large change in the vibrational contribution at T_g must therefore be admitted, which cannot be accounted for by the free volume function h derived from the experimental P–V–T surface.[34] Similarly, only 42% of the entropy difference between the glass and the undercooled liquid at 0 °C are computed. A detailed discussion is found in ref 23. The important implication is that a single structural parameter (here h), not necessarily a constant, which determines the $P(V,T)$ surface, is not sufficient to describe the corresponding entropy surface $S(V,T)$. This is consistent with a result of phenomenological theory,[27] which requires more than a single ordering parameter to describe the observed changes at the transition. A different conclusion is reached for polystyrene by Oels and Rehage.[35]

If our original assumption is to be modified and a second structure function introduced within the frame of the present theory, the only choice is the scaling temperature T^* or c, since the other parameters are defined by the segmental potential solely. Whereas the derivatives of h are reduced in the transition, an increase in T^* and a decrease in c with decreasing temperature must be admitted, in contrast with the constancy for $T > T_g$. This is not unreasonable as an expression of the conformational freeze-in of molecular motion. It would also be consistent with the enhanced sensitivity of C_P to temperature changes observed in the glass near T_g. According to this assumption, the glass would find itself at a lower reduced temperature for a given T than the corresponding liquid and thus ΔC_P would be larger than computed otherwise. In the absence of such an effect, the theory furthermore predicts a lower enthalpy for the densified glass. This is contrary to observation, which would therefore require an increase of c by pressurization. The values derived above from the h function at constant c represent then free volume contributions to ΔC_P and ΔC_V.

(III) Conclusions

(A) The Liquid State. The theory has provided a quantitatively successful equilibrium description of the P–V–T function. Alternative analytical approaches would hardly improve the agreement with experiment but could provide a better foundation or critique of assumptions underlying the present results. An extension of the theory based on molecular distribution functions in its various approximate versions to chain molecular liquids is indicated.[36a] An obvious alternative is computer simulations.[36b] These can be particularly pertinent in connection with the question of external vs. internal degrees of freedom, i.e., the relation between chain flexibility and configurational thermodynamics and short-range order as well.

(B) The Glassy State. We have noted that the extent of freeze-in varies with the location of the reduced glass temperature, as does the unoccupied volume fraction h at T_g. These results suggest a consideration of the hole size or cluster distribution at and below T_g. In polymers with a low T_g, where h is small, this distribution is narrow and it broadens as T_g increases.[13] A partial relaxation of the restraint condition, eq 3, is indicated, which considers the contributions of hole clusters of different sizes to the configurational free energy and freezes the smallest size. This would define a *frozen* ordering parameter in the sense of phenomenological theory. It remains then to be seen to what extent such an assumption reproduces the experimental h function. The question of entropy vs. volume surfaces and transition lines requires careful experimentation with concomitant systematic variations of formation histories. Such results make it possible to examine our proposals in respect to the theoretical quantities h and c. It should be added that any structural investigation of glasses generated by differing thermal histories will be of significance in this context.

The question of predicting a glass transition and the accompanying kinetics from the assumed molecular characteristics of the system remains as a challenge and can perhaps most fruitfully be attacked by molecular dynamics simulation.

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Notes and References

(1) Dedicated to Maurice L. Huggins on the occasion of his 80th birthday.

(2) I. Prigogine, N. Trappeniers, and V. Mathot, *Discuss. Faraday Soc.*, **15,** 93 (1953); I. Prigogine, "The Molecular Theory of Solutions", North-Holland Publishing Co., Amsterdam, 1957.
(3) (a) R. Simha and S. T. Hadden, *J. Chem. Phys.*, **25,** 702 (1956); (b) S. T. Hadden and R. Simha, *ibid.*, **36,** 1104 (1962); (c) *J. Chem. Eng. Data*, **7,** 444 (1962).
(4) R. Simha and A. J. Havlik, *J. Am. Chem. Soc.*, **86,** 197 (1964).
(5) (a) V. S. Nanda and R. Simha, *J. Phys. Chem.*, **68,** 3158 (1964); (b) *J. Chem. Phys.*, **41,** 3870 (1964).
(6) V. S. Nanda, R. Simha, and T. Somcynsky, *J. Polym. Sci., Part C*, **12,** 277 (1966).
(7) R. Simha and T. Somcynsky, *Macromolecules*, **2,** 342 (1969).
(8) Such a superposition has been performed for crystalline systems in a treatment of the conformational contribution to the crystal–melt transition: F. Boyle, P. L. Taylor, A. J. Hopfinger, and R. Simha, *J. Appl. Phys.*, **46,** 4218 (1975).
(9) H. Eyring, D. Henderson, B. J. Jones, and E. W. Eyring, "Statistical Mechanics and Dynamics", Wiley, New York, N.Y., 1964.
(10) D. Chandler and H. C. Andersen, *J. Chem. Phys.*, **57,** 1930 (1972).
(11) R. Simha, J. M. Roe, and V. S. Nanda, *J. Appl. Phys.*, **43,** 4312 (1972).
(12) V. S. Nanda, private communication; Y. R. Midha and V. S. Nanola, *Macromolecules*, **10,** 1031 (1977).
(13) O. Olabisi and R. Simha, *Macromolecules*, **8,** 211 (1975).
(14) R. Simha, P. S. Wilson, and O. Olabisi, *Kolloid Z. Z. Polym.*, **251,** 402 (1973).
(15) (a) P. S. Wilson and R. Simha, *Macromolecules*, **6,** 902 (1973); (b) R. Simha and P. S. Wilson, *ibid.*, **6,** 908 (1973).
(16) F. Bueche, "Physical Properties of Polymers", Interscience, New York, N.Y., 1962.
(17) M. Litt, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **14,** 109 (1973).
(18) O. Olabisi and R. Simha, *J. Appl. Polym. Sci.*, **21,** 149 (1977).
(19) J. E. McKinney and R. Simha, *Macromolecules*, **7,** 894 (1974).
(20) P. Zoller, private communication; *J. Appl. Polym. Sci.*, to be published.
(21) (a) A. Quach and R. Simha, *J. Appl. Phys.*, **42,** 4592 (1971); (b) A. Quach, P. S. Wilson, and R. Simha, *J. Macromol. Sci. Phys.*, **9** (3), 533 (1974).
(22) O. Olabisi and R. Simha, *Macromolecules*, **8,** 206 (1975).
(23) J. E. McKinney and R. Simha, *Macromolecules*, **9,** 430 (1976).
(24) V. S. Nanda and R. Simha, *J. Chem. Phys.*, **41,** 1884 (1964).
(25) J. E. McKinney and R. Simha, *J. Res. Natl. Bur. Stand.*, in press; from data of S. Beret and J. M. Prausnitz, *Macromolecules*, **8,** 536 (1975).
(26) J. I. Berg and R. Simha, *J. Non-Cryst. Solids*, **22,** 1 (1976).
(27) M. Goldstein, *J. Phys. Chem.*, **77,** 667 (1973).
(28) R. Simha, *Ann. N.Y. Acad. Sci.*, **279,** 2 (1976).
(29) T. Somcynsky and R. Simha, *J. Appl. Phys.*, **42,** 4545 (1971).
(30) A. Quach and R. Simha, *J. Phys. Chem.*, **76,** 416 (1972).
(31) J. E. McKinney, *Ann. N.Y. Acad. Sci.*, **279,** 88 (1976).
(32) For example, J. M. Roe and R. Simha, *Int. J. Polym. Mater.*, **3,** 193 (1974); (b) S. Lee and R. Simha, *Macromolecules*, **7,** 909 (1974).
(33) N. I. Shishkin, *Sov. Phys.-Solid State* (*Engl. Transl.*), **2,** 322 (1960).
(34) Such contributions are discussed from a different point of view by M. Goldstein, *Ann. N.Y. Acad. Sci.*, **279,** 68 (1976).
(35) H.-J. Oels and G. Rehage *Macromolecules*, **10,** 1036 (1977).
(36) (a) A start in this direction has been made: J. G. Curro, private communication; (b) *J. Chem. Phys.*, **64,** 2496 (1976).