

A Hole Theory of Polymer Liquids and Glasses. I. Partition Function and Equation of State for Polymer Liquids

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(Received June 15, 1970)

ABSTRACT: The hole theory of simple liquids is applied to polymer liquids and their partition function is derived by application of the method first proposed by Prigogine, *et al.* The equation of state derived does not satisfy the principle of corresponding states. As for the volume dependence of internal pressure at atmospheric pressure, the model where the cell volume is constant gives closer agreement with observed results than the more general model in which the cell volume and the number of holes are both allowed to vary. The molecular parameters needed to check the theory are determined for various polymers.

KEY WORDS Hole Theory / Polymer Liquids / Equation of State /
Corresponding States / Internal Pressure /

Recently various attempts have been made to explain the thermodynamic properties of polymer liquids based on the concept of lattice theory and the theorem of corresponding states.¹⁻¹³ Up to now, two main types of theory have been proposed: one by Prigogine—Simha¹⁻⁹ and the other by Flory.^{10,11} Prigogine—Simha's treatments are based on the lattice theory of simple liquids adapted to polymer systems with some modifications. According to Prigogine,¹ (1) the external degrees of freedom attributable to a segment in a polymeric chain is lower than those for small molecules because of the interconnection of the segments, (2) the occupied volume of a chain segment may be smaller than that of a small molecule for the same reason, and (3) the coordination number becomes smaller as a number of the intermolecular contacts are replaced by intramolecular ones. A new parameter was introduced to characterize such decrease in the external degrees of freedom, in addition to the parameters ordinarily used in the thermodynamics of simple liquids, *e.g.*, the coordination number z , the occupied volume σ^3 , and the intermolecular interaction parameter ϵ^* as used in the Lennard-Jones Devonshire liquid theory.¹⁴ The treatments of most of the other investigators¹⁰⁻¹² are also essentially the

same as Prigogine's regarding the method of evaluating the effects of the interconnection of segments. In these treatments the theorem of corresponding states was assumed for all kinds of molecules and the effects of the interconnection of the segments were introduced only through the characteristic molecular parameters. In the treatment of DiBenedetto¹³ based on the cell model, however, the cell potential energy for amorphous polymers was evaluated by *cylindrically* symmetric potential, and therefore the theorem of corresponding states may be unsatisfactory for different shapes of molecules including spherical and chain molecules.

Throughout this series of papers we are mainly concerned about understanding the differences in thermodynamic properties of polymers between the liquid and glassy states. For this purpose, we adopt the hole theory here and apply it to polymer liquids and glasses.* In our opinion, the cell model, such as proposed by Prigogine and Simha, where all the lattice sites are occupied

* Simha, *et al.*,⁹ have also applied the hole theory to both spherical and chain molecules, in order to improve the cell model for the liquid state by the introduction of spaces in the lattice. They have made no attempt, however, to apply it to polymer glasses.

by segments, may be unable to distinguish the glassy state from the liquid state, and Flory's theory may also be unsuitable to apply to polymer glasses because the structural features of the model do not seem to be clear enough. On the other hand, by the introduction of holes, or empty lattice sites, it may be possible to more readily define the liquid and glassy states as different states in terms of the freezing of holes. The hole model may provide a new approach to the study of glass-transition phenomena.

In this paper we apply the hole theory of simple liquids to polymer liquids according to Prigogine's treatment described above, and present a partition function and the equation of state in the liquid state derived therefrom. Cohesive energy density and internal pressure are also derived and compared with experimental results. The first of the problems to be discussed is the applicability of the hole model to internal pressure. Prigogine and Simha's theory⁷ cannot satisfactorily explain the observed behavior of internal pressure P_i , whereas in Flory's theory¹⁰ the empirical relation $P_i \propto V^{-2}$ is assumed (V , volume). The second problem is to estimate the contribution made by the configuration of polymer chains arranged on the lattice to the equation of state. Such a contribution does not appear in the usual lattice model having no hole.

THEORY

Partition Function

We now consider a system in which N/r polymer molecules, each consisting of r segments, are arranged on a lattice comprising M sites ($M \geq N$), and therefore there remain $M - N$ empty sites or holes. Following Prigogine,¹ we let $3cN$ denote the total number of external degrees of freedom. The partition function for such a system may then be written¹⁵

$$Z = J(T) q^{cN} \sum_{\lambda} g_{\lambda} \left(\prod_i v_r^{(i\lambda)} \right)^c \exp(-U_{0\lambda}/kT) \quad (1)$$

where $J(T)$ is the partition function associated with the intrasegmental degrees of freedom, q^{cN} represents the kinetic part of the partition function associated with the external degrees of freedom when the partition function is handled

classically. In eq 1, λ indicates a given configuration of N segments arranged on M lattice sites and g_{λ} is the number of such configurations. The term $v_r^{(i\lambda)}$ is the free volume of the i -th segment and $U_{0\lambda}$ the intersegmental potential energy of the system associated with the configuration λ when all segments rest at the centers of the cell. If we let $\omega_i^{(i\lambda)}$ denote the fraction of empty sites of the nearest neighbors of the i -th segment, then $v_r^{(i\lambda)}$ and $U_{0\lambda}$ are expressed by

$$v_r^{(i\lambda)} = \int_{\text{cell}} \exp[-(1 - \omega_i^{(i\lambda)})z' \{\varphi(\rho) - \varphi(0)\}/kT] d\rho \quad (2)$$

$$U_{0\lambda} = z' \varphi(0) \left(N - \sum_i \omega_i^{(i\lambda)} \right) / 2 \quad (3)$$

where z' is the average coordination number for a segment, which may be related to the coordination number z of a lattice site by the equation¹

$$z' = (zr - 2r + 2)/r = (z - 2) + 2/r \quad (4)$$

and $z' \varphi(\rho)$ is the average potential energy of a segment at distance ρ from the center of the cell when all the nearest neighbor sites are occupied. It is customary to assume that^{15,16}

$$\ln v_r = \omega \ln v_{r1} + (1 - \omega) \ln v_{r0} \quad (5)$$

Here v_{r1} and v_{r0} are the parameters to be determined arbitrarily to represent v_r most satisfactorily in the range of ω considered and are not necessarily equal to v_r at $\omega = 1$ and 0. Introducing these relations into eq 1, we have

$$Z = J(T) q^{cN} v_{r0}^{cN} \exp\{-z' \varphi(0) N / 2kT\} \times \sum_{\lambda} [g_{\lambda} (v_{r1}/v_{r0})^{c \sum_i \omega_i^{(i\lambda)}/z'} \exp\{\varphi(0) n_{01} / 2kT\}] \quad (6)$$

where $n_{01} = z' \sum_i \omega_i^{(i\lambda)}$ is the number of segment-hole contact pairs. Here we use Bragg-Williams' zero-th approximation¹⁶ for the summation, from which we have

$$\sum_{\lambda} g_{\lambda} (v_{r1}/v_{r0})^{c \sum_i \omega_i^{(i\lambda)}/z'} \exp\{\varphi(0) n_{01}^* / 2kT\} \sum_{\lambda} g_{\lambda} \quad (7)$$

$$= (v_{r1}/v_{r0})^{c n_{01}^* / z'} \exp\{\varphi(0) n_{01}^* / 2kT\} \sum_{\lambda} g_{\lambda}$$

where the value of n_{01}^* , which is the most probable value of n_{01} , may be obtained by applying Guggenheim's theory¹⁷ for mixture systems to be

given by

$$n_{01}^* = z'N(M-N)z / \{(M-N)z + z'N\} \quad (8)$$

Applying Flory's lattice theory¹⁶ of polymer solutions, we have

$$\sum_{\lambda} g_{\lambda} = \{(z-1)/e\}^{(r-1)N/r} M^{N/r} M^{-N} \times (M-N)^{-1} (N/r)^{-N/r} \quad (9)$$

We further define $V = Mv^*$, $V^* = Nv^*$ and thus $\tilde{V} \equiv V/V^* = M/N$, where v^* represents the volume of a cell. The partition function finally assumes the form:

$$\begin{aligned} Z = & J(T) q^{eN} v_{t0}^{eN} \exp\{-z'\varphi(0)N/2kT\} \{(z-1)/e\}^{(r-1)N/r} \\ & \times r^{N/r} (v_{t1}/v_{t0})^{eN(\tilde{V}-1)/(\tilde{V}-1+s)} \tilde{V}^{N(\tilde{V}-1)+N/r} \\ & \times (\tilde{V}-1)^{-N(\tilde{V}-1)} \\ & \times \exp\{N\varphi(0)z'(\tilde{V}-1)/2kT(\tilde{V}-1+s)\} \quad (10) \end{aligned}$$

where $s = z'/z$.

Potential Energy, Free Volume, and Cell Volume

According to the L-J-D theory,¹⁴ the cell energy as a function of V , $U_0(V)$, may be written

$$U_0(V) = z\varepsilon^* \{A(\sigma^3 N/V)^4 - B(\sigma^3 N/V)^2\} / 2 \quad (11)$$

where $A = 1.0109$, $B = 2.4090$ for hexagonal packing. Here ε^* and σ are the characteristic parameters in L-J 12-6 potential, representing respectively the minimum potential energy and the distance of the zero potential which is related to the distance r^* of the minimum potential by $\sigma = 2^{-1/6}r^*$. Although, in the present theory, only the pair of nearest neighbors is taken into account to estimate the intersegmental interactions, $\varphi(0)$ may be better approximated by $2U_0(V^*)/z$ which is derived by taking account of the interactions with molecules, including those beyond the first neighbors. Therefore we may write

$$\begin{aligned} K & \equiv -\varphi(0)/2\varepsilon^* \\ & = -\{A(\sigma^3 N/V^*)^4 - B(\sigma^3 N/V^*)^2\} / 2 \quad (12) \end{aligned}$$

For the sake of simplicity, the potential $\varphi(\rho) - \varphi(0)$ is here approximated by the square well potential, or the smoothed potential,¹ which is expressed by

$$\varphi(\rho) - \varphi(0) = \begin{cases} \infty & \rho > a - \sigma \\ 0 & 0 \leq \rho \leq a - \sigma \end{cases} \quad (13)$$

where a is the mean distance between the first

neighbors. Then, the free volume v_t for $\omega = 0$ is given in this approximation by

$$\begin{aligned} v_t & = \int_{\text{cell}} \exp[z'(-\varphi(\rho) + \varphi(0))/kT] d\rho \\ & = (4\pi/3)(a-\sigma)^3 \quad (14) \end{aligned}$$

If v_{t0} and v_{t1} are taken to be the free volumes when $\omega = 0$ and 1 respectively, we have, from eq 14,

$$v_{t1} = v_t(\omega = 1) = v^* = V^*/N \quad (15)$$

$$\begin{aligned} v_{t0} & = v_t(\omega = 0) \\ & = (4\pi^{1/2}/3) \{1 - 2^{-1/6}(\sigma^3 N/V^*)^{1/3}\}^3 V^*/N \quad (16) \end{aligned}$$

Here the relation $a^3/2^{1/2} = v^*$ valid for hexagonal packing is assumed.

Up to this stage we may choose the cell volume v^* arbitrarily; in other words the number of lattice sites M of the system. It is therefore necessary to indicate the conditions under which it will be decided. It is reasonable to determine the cell volume so as to minimize the free energy F of the system:

$$(\partial F / \partial V^*)_{T, V, N} = -kT(\partial \ln Z / \partial V^*)_{T, V, N} = 0 \quad (17)$$

with this assumption, it now becomes possible to obtain the equation of state for the cell volume.

Equation of State

The equation of state can be derived from the partition function in the conventional manner:

$$\begin{aligned} P & = kT(\partial \ln Z / \partial V)_{T, N} \\ & = kT(\partial \ln Z / \partial V)_{T, V^*, N} \\ & \quad + kT(\partial \ln Z / \partial V^*)_{T, V, N} (\partial V^* / \partial V)_{T, N} \end{aligned}$$

On the basis of eq 17, this equation reduces to

$$P = kT(\partial \ln Z / \partial V)_{T, V^*, N} \quad (18)$$

Substituting in eq 10 and defining $\tilde{T} \equiv T/T^* \equiv ckT/\varepsilon^*z'$ and $\tilde{P} \equiv Pv^*/\varepsilon^*z'$, we have

$$\begin{aligned} \tilde{P} & = (\tilde{T}/c\tilde{V})(1/r-1) + (\tilde{T}/c) \ln(1-1/\tilde{V})^{-1} \\ & \quad + s \ln(v_{t1}/v_{t0})(\tilde{V}-1+s)^{-2} \tilde{T} \\ & \quad - Ks(\tilde{V}-1+s)^{-2} \quad (19) \end{aligned}$$

where $\ln(v_{t1}/v_{t0})$ is given by eq 15 and 16, and K by eq 12. Substituting in eq 17, and using eq 18, we obtain

$$\begin{aligned} \tilde{P}/\tilde{T} & = \tilde{V}^{-1}(\partial \ln v_{t0} / \partial \ln V^*)_{T, V, N} + (1-\tilde{V}^{-1}) \\ & \quad \times (\tilde{V}-1+s)^{-1} [\partial \ln(v_{t1}/v_{t0}) / \partial \ln V^*]_N \\ & \quad + \tilde{T}^{-1} s (\tilde{V}-1+s)^{-1} (\partial K / \partial \ln V^*)_N \quad (20) \end{aligned}$$

By use of eq 12, 15, and 16, eq 20 reduces to

$$\begin{aligned} & \bar{P}(\bar{V}-1+s)/\bar{T}s \\ & = 2^{-1/6}(\sigma^3 N/V^*)^{1/3} (1-2^{-1/6}(\sigma^3 N/V^*)^{1/3})^{-1} \\ & + (\bar{V}-1+s)^{-1} - \{B(\sigma^3 N/V^*)^2 \\ & - 2A(\sigma^3 N/V^*)^4\}/\bar{T} \end{aligned} \quad (21)$$

The combination of eq 19 and 21 gives the equation of state, *i.e.*, the $P-V-T$ relation, and the equation of state for the cell volume, *i.e.*, the $P-V^*-T$ relation.

Cohesive Energy Density and Internal Pressure

Internal energy is calculated by

$$\begin{aligned} U & = kT^2(\partial \ln Z/\partial T)_{V,N} \\ & = kT^2\{(\partial \ln Z/\partial T)_{V,V^*,N} \\ & + (\partial \ln Z/\partial V^*)_{V,T,N}(\partial V^*/\partial T)_{V,N}\} \\ & = kT^2(\partial \ln Z/\partial T)_{V,V^*,N} \end{aligned} \quad (22)$$

where V^* must satisfy eq 17. Thus, cohesive energy density D and internal pressure P_i are given by

$$D \equiv (U^0 - U)/V = -(kT^2/V)(\partial \ln Z_V/\partial T)_{V,V^*,N} \quad (23)$$

$$\begin{aligned} P_i & \equiv (\partial U/\partial V)_T = -(\partial(VD)/\partial V)_T \\ & = kT^2\{(\partial \ln Z_V/\partial T)_{V,V^*,N}(\partial V)_T \} \end{aligned} \quad (24)$$

where U^0 is the internal energy of the system in the state where no intersegmental interactions existed; U is that in the liquid state considered, and Z_V is the volume dependent part of Z , *i.e.*, $\sum_{\lambda} g_{\lambda} (\prod_i v_i^{i\lambda})^c \exp(-U_{0\lambda}/kT)$. Substituting the expression for Z_V (eq 10) in eq 23 and 24, we have

$$\bar{D} \equiv Dv^*/\varepsilon^*z' = Ks\bar{V}^{-1}(\bar{V}-1+s)^{-1} \quad (25)$$

$$\begin{aligned} \bar{P}_i & \equiv P_iv^*/\varepsilon^*z' \\ & = Ks(\bar{V}-1+s)^{-2} (1-\bar{V}(\partial V^*/\partial V)_T) \\ & - (\bar{V}-1+s)^{-1} V^*(\partial K/\partial V^*)(\partial V^*/\partial V)_T \end{aligned} \quad (26)$$

Here $(\partial V^*/\partial V)_T$ may be obtained by transforming the relation

$$(\partial V^*/\partial T)_P = (\partial V^*/\partial T)_V + (\partial V^*/\partial V)_T(\partial V/\partial T)_P \quad (27)$$

to

$$(\partial V^*/\partial V)_T = h(1 - (\partial V^*/\partial T)_V / (\partial V^*/\partial T)_P) / \bar{V} \quad (27')$$

where

$$h \equiv (\partial \ln V^*/\partial T)_V / (\partial \ln V/\partial T)_P$$

Differentiating eq 18 with respect to temperature at constant pressure and constant volume, and

using the relation $P_i + P = T(\partial P/\partial T)_V$, we have

$$\begin{aligned} & (\partial V^*/\partial V)_V / (\partial V^*/\partial T)_P \\ & = \{P_i \bar{V}(\bar{V}-1+s)/s + V^*(\partial K/\partial V^*)_N\} \\ & \times \{V^*(\partial K/\partial V^*) - P\bar{V}(\bar{V}-1+s)/s \\ & + P(2\bar{V}-1+s)/sV^*\}^{-1} \end{aligned} \quad (28)$$

At atmospheric pressure $P=0$. Hence it follows from eq 26, 27, and 28 that the reduced internal pressure is finally given by

$$\begin{aligned} \bar{P}_i & = Ks(\bar{V}-1+s)^{-2} (1-h-h\bar{V}(\bar{V}-1+s)^{-1} \\ & \times (\partial \ln K/\partial \ln V^*)^{-1})^{-1} \end{aligned} \quad (29)$$

When there is no hole, *i.e.*, $\bar{V}=1$ and $h=1$, eq 29 reduces to $\bar{P}_i = (\partial K/\partial \ln V^*)_N$, which is the result obtained from Simha's theory.⁷

Constant Cell Volume Model

For simplicity, let us now consider the case where the cell volume is constant, being independent of temperature and pressure. As can be seen from eq 18 and 22, the equation of state and the internal energy (hence cohesive energy density) can thus be expressed in the form identical with that in the case of the changeable cell volume model, *i.e.*, expressed by eq 19 and 25. Internal pressure is however, given by a simpler form,

$$\bar{P}_i = P_iv^*/\varepsilon^*z' = Ks(\bar{V}-1+s)^{-2} \quad (30)$$

because $(\partial V^*/\partial V)_T = 0$ in eq 26. For numerical calculations we assume $V^* = \sigma^3 N$.

COMPARISON WITH EXPERIMENTAL OBSERVATIONS

Previous investigators have often evaluated the molecular parameters so that the theory considered agreed with experimental data for such factors as volume-temperature relation and cohesive energy density. Considering the fact, however, that there exists no satisfactory theory even for simple liquids, we think it would be preferable to determine the parameters without the aid of any particular theoretical model and examine a theory with the parameters thus obtained (although even in this case some assumptions and approximations may be necessary). We use here the following method of estimating the parameters, considering that reasonable values of a characteristic volume $\sigma^3 N$, or the volume

of hypothetical liquid at 0°K, V_0 , may be estimated comparatively easily by the use of data for crystals or gases. In the present theory, V_0 and $\sigma^3 N$ are related with each other by the equation $V_0 = (2A/B)^{1/2} \sigma^3 N = 0.9161 \sigma^3 N$; this is derived from the condition $\partial U_0 / \partial V = 0$ with eq 11. First we determined the value V_0 according to Miller's estimate,¹⁹ assuming the additivity of the characteristic volumes of atomic groups. In Figure 1, $\log V/\sigma^3 N$ is plotted against $\log T$ for various compounds with the use of the characteristic volume thus obtained. We assume here the principle of corresponding states for the equation of state. We believe this assumption a reasonable one in determining parameters since no satisfactory equation of state is as yet available. Since the values of ϵ^* and σ^3 for argon¹⁵ are obtainable with a high degree of reliability from the second virial coefficient, the curve for argon can be taken as a reference. The curves of $\log V/\sigma^3 N$ vs. $\log T$ for other compounds are shifted on to that of argon to evaluate their T^*

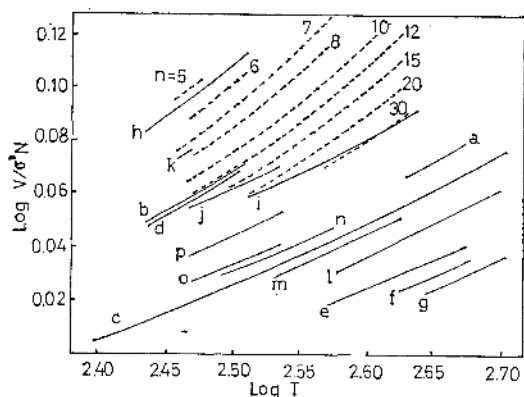


Figure 1. $\log V^*/\sigma^3 N$ vs. $\log T$ curves: ----, n -hydrocarbons (n , carbon number); a, polyethylene (Sholex)²⁰; b, ethyl benzene²¹; c, polystyrene²²; d, Isopropylbenzene²¹; e, poly(α -methylstyrene)²³, $\bar{p}=11.9$; f, $\bar{p}=33.1$; g, $\bar{p}=5000$; h, ethyl acetate²¹; i, poly(vinyl acetate)²⁰; j, poly(ethyl acrylate)²⁴; k, ethyl isobutylate²⁵; l, poly(methyl methacrylate)²⁶; m, poly(ethyl methacrylate)²⁶; n, poly(n -propyl methacrylate)²⁶; o, poly(n -butyl methacrylate)²⁶; p, polyisobutylene.²⁴

Table I. Molecular parameters

Substance	V_0 , cc/g	V , cc/g (at °C)	E^* , cal/cc	T^* , 10 ³ °K	$\sigma^3 N/c$, cc/mol	$1/c$
Ethylbenzene ^a	0.925	1.152 (20)	112.2	5.80	78.3	0.73 ⁺
Polystyrene ^b ($\bar{p}=3.1$)	0.845	0.964 (20)	112.2	8.66	124.6	
Polystyrene ^b (high M. W.)	0.808	0.968 (98)	112.2	8.66	128.8	1.40
iso-Propylbenzene ^a	0.934	1.160 (20)	105.1	5.84	84.2	0.69 ⁺
Poly(α -methylstyrene) ^c	0.830	0.952 (165)	105.1	12.49	197.9	1.85
Ethyl acetate ^a	0.812	1.110 (20)	149.2	4.50	47.9	0.61 ⁺
Poly(vinyl acetate) ^d	0.678	0.836 (25)	149.2	6.15	68.5	1.08
Poly(ethyl acrylate) ^e	0.723	0.894 (20)	138.2	6.11	73.7	0.93
Methyl isobutylate ^f	0.863	1.122 (20)	138.2	6.41	73.6	0.77 ⁺
Poly(methyl methacrylate) ^g	0.740	0.870 (105)	138.2	9.69	117.0	1.45
Poly(ethyl methacrylate) ^g	0.772	0.900 (65)	130.9	9.05	115.2	1.20
Poly(n -propyl methacrylate) ^g	0.797	0.929 (35)	125.9	8.24	109.1	0.98
Poly(n -butyl methacrylate) ^g	0.817	0.948 (20)	122.0	8.00	109.2	0.90
n -Octane ^a	1.105	1.423 (20)	96.8	5.16	85.5	0.62 ⁺
Polyisobutylene ^o	1.000	1.187 (20)	96.8	7.14	122.9	2.01
Polyethylene (Sholex) ^h	1.000	1.268 (150)	96.8	7.93	136.4	4.46

^a G. Allen, *et al.*²¹ ^b K. Ueberreiter and G. Kanig,²² ^c T. Yasuda and T. Hata,²³ ^d G. Allen, *et al.*²⁷ ^e G. Allen, *et al.*²⁴ ^f J. H. Perry,²⁵ ^g S. S. Rogers and L. Mandelkern,²⁶ ^h S. Kitagawa and T. Hata.²⁰ ⁺, the value of $1/c$ per molecule.

The values of no signs are $1/c$ per their respective repeating unit.

To calculate z' from eq 4, r is taken as 2 for ethylbenzene and iso-propylbenzene, 4 for ethylacetate and methylisobutylate, 6 for polystyrene $\bar{p}=3.1$, 8 for n -octane, and ∞ for the other substances. The values E^* for poly(ethyl acrylate) and poly-methacrylates are evaluated from E^* of ethylacetate and n -octane by the equation $E^{*1/2} = \theta_1 E_1^{*1/2} + \theta_2 E_2^{*1/2}$, where θ_i denotes the characteristic-volume fraction, *i.e.*, $\theta_i = \sigma_i^3 / (\sigma_1^3 + \sigma_2^3)$, and the subscripts 1 and 2 refer to ethylacetate and n -octane, which will be discussed in a paper later in this series.

($\equiv \varepsilon^* z' / ck$) from the shift factors and the T^* value for argon which is evaluated with $c=1$ and $z=12$. The value of $\varepsilon^* z' / \sigma^3 N$ can be determined from eq 25 with experimental values of cohesive energy density, volume, and the characteristic volume obtained above. Here we use $V^* = \sigma^3 N$, because as regards cohesive energy density the difference between the two models, i.e., $V^* = \sigma^3 N = \text{constant}$ and $V^* = \text{changeable}$, is within 2% in the range of \tilde{V} treated in the present calculation. The value of E^* defined as $K\varepsilon^* z' / \sigma^3 N (=0.699\varepsilon^* z' / \sigma^3 N$ in the case of $V^* = \sigma^3 N$ from eq 12) is calculated from $\varepsilon^* z' / \sigma^3 N$ obtained here and z'/z which is determined from eq 4 with $z=12$ and the value of r chosen appropriately (see the bottom of Table I). Now, with the values of T^* and $\varepsilon^* z' / \sigma^3 N$ being known, we can evaluate a molar volume of freely movable segment $\sigma^3 N/c$, i.e., the volume of a unit which has three external degrees of freedom. The molecular parameters thus derived are tabulated in Table I. In the last column of Table I, we show the values of $1/c$ for a repeating unit taken as a segment, which represent the ratios of the volume $\sigma^3 N/c$ to the volume $\sigma^3 N$ of a repeating unit. In poly(*n*-alkyl methacrylates), the value of $1/c$ for a repeating unit decreases with increasing the chain length of the side group. The value of $1/c$ for polyethylene is very large and more than twice that for polyisobutylene. These results suggest that the external degree of freedom is greatly affected by the freedom of side groups as well as the rotational hindrance about chain backbones.

Volume-Temperature Relation at Zero Pressure

If we put $\tilde{V} = V/V^* = 1$ in eq 21, then eq 21 reduces to the equation of state in Simha's theory.⁷ The solid and broken lines in Figure 2 show theoretical curves of $V/\sigma^3 N$ vs. \tilde{T} and $V^*/\sigma^3 N$ vs. \tilde{T} at atmospheric pressure calculated from eq 19 and 21; here, we may assume $PV^*/cNkT \equiv \tilde{P}/\tilde{T} \ll 1$. The theoretical curves of $V/\sigma^3 N$ vs. \tilde{T} for the constant cell volume are also shown by chain lines in Figure 2; these have been calculated from eq 19 with $K=(B-A)/2=0.699$ and $\ln(v_{11}/v_{10})=4.87$ which are obtained from eq 12, 15, and 16 with $V^* = \sigma^3 N$. The $V/\sigma^3 N$ vs. \tilde{T} relations for both models vary with c and r . Thus the principle of correspond-

ing states does not hold for the equation of state. The equation of state for polymer liquids may be quite different from that of low-molecular weight liquids, since c and $1/r$ for the former may be much smaller than those for the latter. On the other hand, the $V^*/\sigma^3 N$ vs. \tilde{T} relation is virtually independent of c and r , because

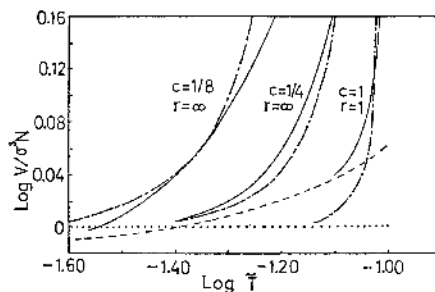


Figure 2. Calculated curves of volume— and cell volume—temperature relations at atmospheric pressure. The curves indicated by the solid and broken lines are, respectively, $\log V/\sigma^3 N$ and $\log V^*/\sigma^3 N$ against $\log \tilde{T}$ derived from the changeable cell volume model (eq 19 and eq 21), and the curves shown by chain lines are $\log V/\sigma^3 N - \log \tilde{T}$ relations for the constant cell volume model (eq 19) when the cell volume V^* is $\sigma^3 N$ being indicated by the dotted line.

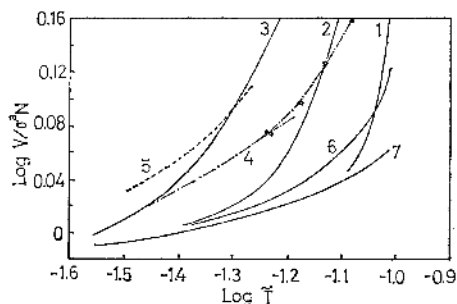


Figure 3. $\log V/\sigma^3 N$ vs. $\log \tilde{T}$ curves at atmospheric pressure for some theories and experimental results: 1, the present theory (the changeable cell volume model), $r=1$ and $c=1$; 2, $r=\infty$ and $c=1/4$; 3, $r=\infty$ and $c=1/8$; 4, the experimental curve of the present analysis (a part of the curve deviated downward from the main curve in the vicinity of $\log \tilde{T} = -1.20$ is that for polymers); ●, liquid argon;¹⁵ ○, liquid methane²⁸; 5, Flory's theory,¹⁰ putting $\tilde{T}(\text{Flory}) = \tilde{T}/0.718$ and $\tilde{V}(\text{Flory}) = V/V_0$; 6, Simha's theory of harmonic oscillation⁶; 7, Simha's theory of square well potential.⁷

the left hand side of eq 21 may be ignored at atmospheric pressure, and the second term on the right hand side involving \bar{V} and s is smaller than the preceding term and the variation of \bar{V} and s has almost no effect on the $V^*/\sigma^3 N$ vs. \bar{T} relation.

The curves of $\log V/\sigma^3 N$ vs. $\log \bar{T}$ derived from the present theory and others are compared with experimental data in Figure 3. None of the theoretical curves fit the experimental results over a wide range of temperature. The $\log V/\sigma^3 N$ vs. $\log T$ curves either for polymers or for simple liquids are roughly superposable on each other. Experiments indicate that as the molecule becomes longer or as the external degrees of freedom per segment decrease, the slope of the $\log V/\sigma^3 N$ vs. $\log T$ curve tends to decrease, as is observed in a series of n -hydrocarbons shown in Figure 1. This similar tendency is reproduced by the hole theory as shown in Figure 2 or 3. The fact that the hole theory does not satisfy the principle of corresponding states is due mainly to the first and second terms on the right hand side of eq 21; these terms arise from the volume dependence of the entropy associated with the configuration of polymer chains arranged on the lattice. Such volume dependence appears as the result of the introduction of holes.

In Figure 4, the $V^*/\sigma^3 N$ vs. \bar{T} curve at zero pressure calculated by eq 21 is shown together with the $V/\sigma^3 N$ vs. \bar{T} curve for the liquid state, which was obtained experimentally beforehand. We obtained the $V/\sigma^3 N$ vs. \bar{T} curve for the glassy state drawn in the figure by converting experimental data for V vs. T to the reduced variables with the same characteristic parameters as those

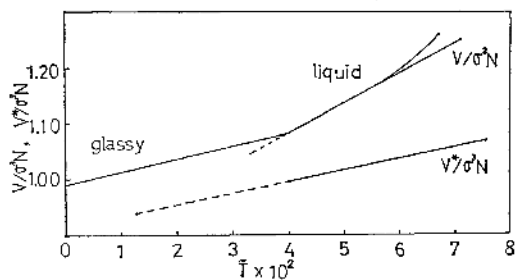


Figure 4. Temperature dependence of volume at atmospheric pressure and that of cell volume: $V/\sigma^3 N$, experimental; $V^*/\sigma^3 N$, calculated.

used in the liquid state, and averaging over several polymers. The slope of the theoretical curve of $V^*/\sigma^3 N$ vs. \bar{T} is almost the same as that of the experimental $V/\sigma^3 N$ vs. \bar{T} curve for the glassy state. The cell volume V^* and the hole volume ($V - V^*$) may correspond to the van der Waals volume and the empty volume given by Bondi,²⁹ respectively. They are also similar, in their temperature dependence, to the occupied volume and the free volume introduced in the free volume theory in polymer rheology.³⁰

Internal Pressure and Cohesive Energy Density

Theoretical curves for internal pressure and cohesive energy density are illustrated in Figure 5. The broken lines show the curves calculated by eq 25 and 29 for the changeable cell volume model. Here the values of h , \bar{V} , and $V^*/\sigma^3 N$ against $V/\sigma^3 N$ are evaluated by the $V/\sigma^3 N$ vs. \bar{T} relation obtained experimentally and the $V^*/\sigma^3 N$ vs. \bar{T} relation shown in Figure 4. The solid lines show the curves for the constant cell volume model calculated from eq 25 and 30 with $K = 0.699$ for $V^* = \sigma^3 N$. In the range of small values of r , the $P_i/\sigma^3/z'\epsilon^*$ vs. $V/\sigma^3 N$ and $D\sigma^3/z'\epsilon^*$ vs. $V/\sigma^3 N$ relation depend on r through s only. Figure 6 shows values of P_i vs. \bar{V} calculated from observed data with the aid of the molecular parameters obtained above. The curves indicated by 1, 2, and 3 in the figure have been derived

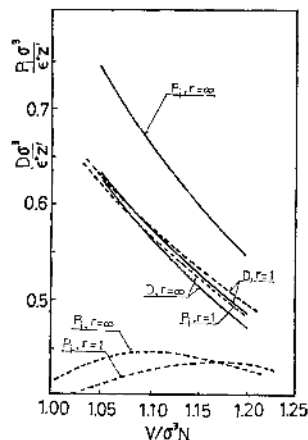


Figure 5. Calculated curves of cohesive energy density and internal pressure at atmospheric pressure. The curves indicated by the broken and solid lines are derived from the changeable cell volume model and the constant cell volume model ($V^* = \sigma^3 N$), respectively.

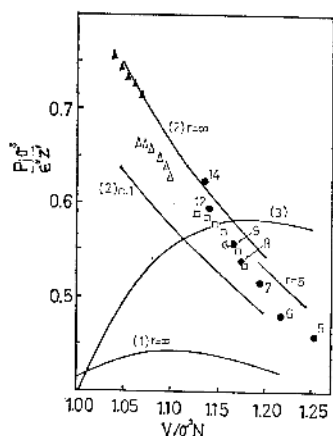


Figure 6. Reduced internal pressure at atmospheric pressure: experimentals, \blacktriangle , oligostyrene²⁴; \triangle , polyisobutylene; \square , poly(ethyl acrylate)²⁴; \circ , poly(vinyl acetate)²⁷; \bullet , *n*-hydrocarbons²¹ (the numbers indicate the carbon number), and calculated (—), 1, the changeable cell volume model; 2, the constant cell volume model; 3, Simha's theory⁷ (with no hole).

from eq 29, 20, and Simha's theory,⁷ respectively. Curve 2 represents the internal pressure arising from the change in the hole fraction when the cell volume is kept constant. Curve 3 represents the internal pressure arising from the change in the cell volume when there is no hole. Curve 1 takes account of the changes in both the hole fraction and the cell volume. The experimental results in this range of $V_i/\sigma^3 N$ are nearer to Curve 2 than Curve 1, corresponding to the model which is thought to be more general. Recalling that the curves of $D\sigma^3/\epsilon^* z'$ vs. $V_i/\sigma^3 N$ for any case in Figure 5 are (almost) the same as Curve 2 in the case where $r=1$, we can see that the ratio P_i/D for Curve 1 is less than unity. In the case where the cell volume is constant the ratio P_i/D is expressed by $\bar{V}_i/(\bar{V}_i - 1 + s)$, which varies in the range 1.0–1.2 for $s=1-10/12$ in accordance with experimental fact.²¹ When a substance in the liquid state is successively compressed, the internal pressure should be zero at a point near V_0 and become negative beyond this point. Thus from this point of view Curve 1 and Curve 3, in which P_i becomes negative with compression, are more realistic than Curve 2 where this does not occur. The model of constant cell volume is, however, more useful

in analyzing experimental results, because it is simpler and leads to closer agreement with experiment in the normal liquid range.

The internal pressures calculated on the constant cell volume model with the molecular parameters shown in Table I are compared with experimental data in Table II. The calculated values are slightly larger than the experimental ones except for oligostyrene. Variation of D , P_i and P_i/D with chain length are shown for *n*-hydrocarbons in Figure 7, where the observed values of P_i , D and their ratios at 20°C are plotted against the reciprocal of the carbon number n and compared with the theoretical

Table II. Comparison of experimental and calculated internal pressures

Substance	$T, ^\circ\text{C}$	$P_i, \text{cal/cc}$	
		Exptl ^a	Calcd
Ethylbenzene	20	84.2	84.3
Oligostyrene	20	102.9	101.4 ^b
Ethyl acetate	20	84.5	92.2
Poly(vinyl acetate)	70	99.0	103.7
Poly(ethyl acrylate)	20	96.2	101.2
Polyisobutylene	20	74.9	78.5

^a G. Allen, *et al.*,^{21,24,27}

^b In this calculation, z' was estimated with $r=6$ in eq 4.

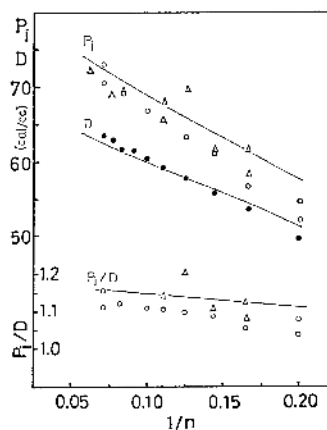


Figure 7. Internal pressure and cohesive energy density of *n*-hydrocarbons at 20°C: —, calculated; and \circ , \bullet , \triangle , experimental (The data shown by \circ and \bullet are those from ref 21). The data for P_i indicated by \triangle are obtained from ref 10 and those for P_i/D indicated by \triangle are calculated with P_i from ref 10 and D from ref 21).

curves calculated on the constant cell volume model. Here the values of V_0 have been estimated by Miller's equation $(14n+14)/(14n-2)$, cc/g.¹⁹ The value of E^* evaluated from the observed D for n -octane at 20°C²¹ (96.8 cal/cc) has been used for other n -hydrocarbons (this value had also been used for polyethylene and polyisobutylene in Table I). The calculated curves compare with experimental results fairly well, indicating that the variation of the reduced volume with chain length is the major factor for the dependence of D and P_1 on the carbon number. The ratio P_1/D slightly increases as the reduced volume V/σ^3N decreases, and extrapolation yields $P_1/D=1.15$ at $n=\infty$.

DISCUSSION

In this paper the V/σ^3N vs. \bar{T} relation obtained experimentally has often been used for calculating theoretical curves, but the partition function (eq 10) failed to reproduce the experimental V/σ^3N vs. \bar{T} relation. The use of the experimental relation implies such a correction for the free energy that the equation of state derived therefrom may satisfy the principle of corresponding states:

$$F_c = F + TS_c(V/V^*)$$

where F and F_c are the free energies before and after the correction. The correction term $S_c(V/V^*)$, which is a function of V/V^* only, does not affect the properties treated here, viz., D , P_1 , and the V^*/σ^3N vs. \bar{T} relation, except for the equation of state (i.e., V/σ^3N vs. \bar{T} relation). The failure of the present theory in the equation of state may arise either from an erroneous estimate of the entropy associated with the configuration of polymer chains, or from that of the "communal entropy" which cannot be estimated by the usual lattice theory. Therefore, since these entropies may depend primarily upon the hole fraction, hence M/N ($=V/V^*$), it may be reasonable to add the entropy S_c , a function of V/V^* , as a correction term, as was done in the above correction. This is consistent with the fact that the present theory gives fairly good results for D , P_1 , and the cell volume, but not for the equation of state.

Acknowledgment. The author wishes to thank

Prof. T. Hata of the Tokyo Institute of Technology for his interest, encouragement, and helpful advice.

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