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Empirical equations of configurational energy and heat capacity for polymer and simple liquids

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The empirical equations of configurational energy $U_{\mathrm{conf.}}$ and configurational heat capacity $C_{\mathrm{P,conf.}}$ have been derived for polymer and simple liquids including amorphous polymer liquids, rare gas liquids, and non-polar and polar liquids based on experimental data over the temperature range up to vapour–liquid critical temperature T_{C}. The equations obtained in this work are:

$$U_{\mathrm{conf.}} = \frac{U_0V_0(V-V^*)}{V(V_0-V^*)}\exp\left(\frac{V^*(V_0-V)}{V(V_0-V^*)}\right)$$

$$C_{\mathrm{P,conf.}} = \frac{U_0V_0V^{*2}\alpha_P(V_0-V)}{V^2(V_0-V*)^2}\exp\left(\frac{V^*(V_0-V)}{V(V_0-V^*)}\right)$$

where V is specific volume, α_P is the thermal expansion coefficient, U_0 is the minimum of $U_{\mathrm{conf.}}$, V^* is V when $U_{\mathrm{conf.}} = 0$, and V_0 is V when $U_{\mathrm{conf.}} = U_0$. The expressions of cohesive energy density, internal pressure P_{i} and the V_{m} at which P_{i} is maximum are also obtained based on the equation of configurational energy. The values of V^*, V_0, V_{m} and U_0 used in the above equations are determined for various materials based on the experimental values of thermal pressure coefficient γ_V over a wide range of volume and thermodynamic equation of state given by $(\partial U/\partial V)_T = \gamma_V T - P$. The empirical expressions for $\alpha_P T$ and $\gamma_V V$ are also obtained based on experimental data, which are

$$\ln(\alpha_P T)^{-1} = a_0 + a_1 X$$

$$\ln\frac{\gamma_V V - \gamma_{V_{\mathrm{C}}} V_{\mathrm{C}}}{\gamma_V V} = b_0 + b_1 X + b_2 X^2$$

where $X = \ln((T_{\mathrm{C}} - T)/T)$, γ_V is the thermal pressure coefficient, T_{C} is the critical temperature and $\gamma_{V_{\mathrm{C}}} V_{\mathrm{C}}$ is that at critical point. Values of a_0, a_1, b_0, b_1, and b_2 are constants and are $a_0 = 1.1820$, $a_1 = 0.8425$, $b_0 = -0.1724$, $b_1 = 0.1520$ and $b_2 = -0.0255$ for master curves. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: equation of state; configurational energy; configurational heat capacity)

NOMENCLATURE

PS	Polystyrene
POMS	Poly(orthomethyl styrene)
PVME	Poly(vinyl methyl ether)
PIB	Polyisobutylene
PMMA	Poly(methyl methacrylate)
PNBMA	Poly(*n*-butyl methacrylate)
PCHMA	Poly(cyclohexyl methacrylate)
PC	Polycarbonate
PA	Polyarylate
PH	Phenoxy
PECH	Polyepichlorohydrin

INTRODUCTION

The configurational (or intermolecular) energy $U_{\mathrm{conf.}}$ is an important thermodynamic quantity and is defined by the energy of the liquid minus that of the substance in the perfect gas state[1]. For liquids at ordinary temperature, the vapour is nearly ideal, the $U_{\mathrm{conf.}}$ is thus regarded as the negative of the energy of vaporization ΔE^{V}, i.e. $U_{\mathrm{conf.}} = -\Delta E^{\mathrm{V}}$. In 1924, Lennard-Jones and coworkers[2] proposed an expression for the intermolecular potential based on the assumption of spherical symmetry of molecules:

$$\Phi(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{1}$$

where ε is the minimum of Φ, σ is the distance when $\Phi = 0$ and is regarded as the molecular 'diameter', and r is the distance between a pair of interaction molecules. This equation has been used with great success and is accepted extensively.

The modified form of equation (1) is used in Prigogine's[3] smoothed potential or square well model as

$$U_{\mathrm{conf.}} = U_0\{[A/(\tilde{V})^4] - [B/(\tilde{V})^2]\} \tag{2}$$

which gives configurational heat capacity by

$$C_{\mathrm{P,conf.}} = 2\alpha_P U_0\{[B/(\tilde{V})^2 - 2A/(\tilde{V})^4]\} \tag{3}$$

This model gives good results for reduced cohesive energy

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but poor results for reduced internal pressure as a function of reduced volume[4]. The $C_{P,\mathrm{conf.}}$ is used to analyse the heat of mixing[5a] and gives rather good results in prediction of lower critical solution temperature (LCST) at temperatures below $0.75T_C$[5b].

The van der Waals model for the dependence of $U_{\mathrm{conf.}}$ on volume is also popular, which is expressed by

$$\tilde{U}_{\mathrm{conf.}} = -1/\tilde{V}^n \tag{4}$$

where $\tilde{U}_{\mathrm{conf.}} = U_{\mathrm{conf.}}/U^*$ and $\tilde{V} = V/V^*$ are reduced configurational energy and volume and U^* and V^* are the reduction parameters. This model is mathematically simple, but predicts a monotonic decreasing of $U_{\mathrm{conf.}}$ with increasing volume, so can only be used in a limited volume range.

Flory and collaborators[6–8] have used equation (4) with $n = 1$ for the dependence of configurational energy on volume, i.e.

$$\tilde{U}_{\mathrm{conf.}} = -1/\tilde{V} \tag{5}$$

thus

$$\tilde{C}^{-1}_{\mathrm{P,conf.}} = (1 - 2\tilde{V}^{-1/3}/3) - 2(1 - \tilde{V}^{-1/3})/(\tilde{P}\tilde{V}^2 + 1) \tag{6}$$

The model has obtained good results in applying the resulting equation of state to n-alkanes[6] and in using the model to predict the thermodynamic properties of mixtures of n-alkanes[7] and of quasi-spherical molecules[8–10].

The $U_{\mathrm{conf.}}$ relates to many other thermodynamic quantities of materials such as internal pressure P_{i} and thermal pressure coefficient γ_V. One of the uses for these quantities is to predict the miscibility between polymer and solvent by relating $U_{\mathrm{conf.}}$ to solubility parameter δ in the theories of Hildebrand and Scott[11] and Scatchard[12] by

$$\Delta H_{\mathrm{m}} = V\left\{\left(\frac{\Delta E_1^{\mathrm{V}}}{V_1}\right)^{1/2} - \left(\frac{\Delta E_2^{\mathrm{V}}}{V_2}\right)^{1/2}\right\}^2$$

$$\phi_1\phi_2 = V(\delta_1 - \delta_2)^2\phi_1\phi_2$$

where

$$\delta_i = \left(\frac{\Delta E_i^{\mathrm{V}}}{V_i}\right)^{1/2}$$

is the solubility parameter of species i, V is the volume of the mixture, ΔE_i^{V} is the energy of vaporization of species i, V_i is the molar volume of species i, and ϕ_i is the volume fraction of i in the mixture. The values of δ for polymers cannot be calculated from heat of vaporization data because of their nonvolatility. One of the methods is to determine δ from internal pressure because δ equals the square root of the internal pressure P_i[13]. The quantity $(\delta_1 - \delta_2)^2$ must be extremely small or zero for the mixtures to be miscible in order to make ΔH_{m} a minimum value. Although this is a useful method to predict the solubility, there are a lot of limitations in applications to real solutions over a wide range of temperature and pressure. In Patterson's theory of corresponding state[5b,14], $U_{\mathrm{conf.}}$ and $C_{\mathrm{P,conf.}}$ are used to express the interaction parameter between solvent (1) and polymer (2) by

$$\chi_{12} = \frac{(-U_{\mathrm{conf.}})_1}{RT}\nu^2 + \frac{(C_{\mathrm{P,conf.}})_1}{2R}\tau^2 \tag{7}$$

where $\tau = 1 - (T_1^*/T_2^*)$, and T^* is reduction parameter and can be determined by the equation of state, R is the gas constant and ν^2 corresponds to X_{12}/P_1^* in Flory's theory, where X_{12} is the interaction energy between components 1 and 2. The first term in equation (7) is the contact interactional term which results from the interchange energy for forming contacts between polymer and solvent segments and from differences in the sizes of these segments. Thus $-U_{\mathrm{conf.}}/T$ is a positive decreasing function of T, while the second term is a structural or free volume term due to changes of free volume on mixing the dense polymer liquid with the expanded solvent. Because $C_{\mathrm{P,conf.}}$ is positive and increases with increasing T, and finally goes to infinity at the solvent vapour-liquid critical point, χ_{12} first decreases with T, then passes through a minimum and increases. Therefore, equation (7) can be used to predict the upper critical solution temperature (UCST) and lower critical solution temperature (LCST) in polymer solutions. Hence, more reasonable models for $U_{\mathrm{conf.}}$ and $C_{\mathrm{P,conf.}}$ are desirable in order to predict UCST and LCST accurately, which is the purpose of the present work.

In previous papers[15,16], we have determined the *PVT* properties and thermodynamic quantities such as thermal expansion coefficient α_P, compressibility β_T and thermal pressure coefficient γ_V for amorphous and crystalline polymers accurately based on our equation of state[17–20]. In the present work, we have proposed the empirical equations of $U_{\mathrm{conf.}}$ and its derivatives, such as $C_{\mathrm{p,conf.}}$, P_{i} and cohesive energy density (CED) and the empirical expressions of $\alpha_P T$ and $\gamma_V V$.

DERIVATIONS

We assume the equation for configurational energy as

$$U_{\mathrm{conf.}} = a\left(\frac{V^* - V}{V}\right)\exp\left(b\left(\frac{V^* - V}{V}\right)\right) \tag{8}$$

where a and b are constants, and V^* is the volume when $U_{\mathrm{conf.}} = 0$. The above equation is based on previous work[21], in which we have

$$U = \alpha\exp\left(\int_{V_C}^{V}\frac{Y^{\beta_0}}{V}\mathrm{d}V\right) \tag{9}$$

In the case of $\beta_0 = 1$, U is given by

$$U = \alpha(1 - Y)\exp(-Y) \tag{10}$$

where α is a constant and $Y = (V - V_C)/V$. Equation (10) is modified to equation (8) by taking into account a boundary condition that $U_{\mathrm{conf.}} = 0$ at $V = V^*$. Differentiating equation (8) with respective to V, we obtain

$$\frac{\mathrm{d}U_{\mathrm{conf.}}}{\mathrm{d}V} = -\frac{aV^*\left[1 + b\left(\frac{V* - V}{V}\right)\right]}{V^2}\exp\left(b\left(\frac{V^* - V}{V}\right)\right) \tag{11}$$

By setting equation (11) equal to zero, b is determined and then a is evaluated from equation (8) with a condition $U_{\mathrm{conf.}} = U_0$ at $V = V_0$, where U_0 is the minimum of $U_{\mathrm{conf.}}$ and V_0 is the volume when $U_{\mathrm{conf.}} = U_0$. The constants a and b are given by

$$a = -eU_0V_0/(V_0 - V^*) \tag{12}$$

$$b = V_0/(V_0 - V^*) \tag{13}$$

We can rewrite equation (8), by using equations (12) and (13), as

$$U_{\mathrm{conf.}} = \frac{U_0V_0(V - V^*)}{V(V_0 - V^*)}\exp\left(\frac{V^*(V_0 - V)}{V(V_0 - V^*)}\right) \tag{14}$$

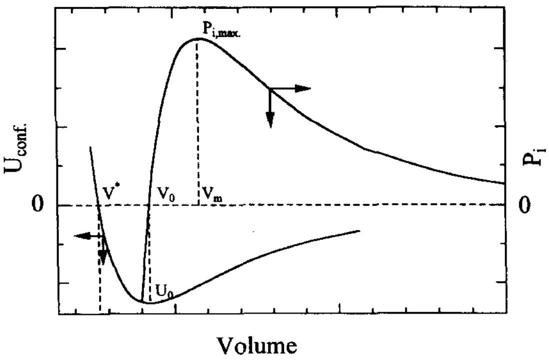

Figure 1 Schematic diagram showing the relationships between V^*, V_0, V_m, U_0, and $P_{i,max}$

The internal pressure P_i is defined by

$$P_i = \left(\frac{\delta U_{conf.}}{\delta V}\right)_T = \gamma_V T - P \tag{15}$$

where it is assumed that $U_{int} = U_{conf.} + U(T)$, configurational heat capacity $C_{P,conf.}$ is defined by

$$C_{P,conf.} = \left(\frac{\delta U_{conf.}}{\delta T}\right)_P \tag{16}$$

CED is defined by

$$\text{CED} = -U_{conf.}/V \tag{17}$$

and they are obtained by using equation (14) as

$$P_i = \frac{U_0 V_0 V^{*2}(V_0 - V)}{V^3(V_0 - V^*)^2}\exp\left(\frac{V^*(V_0 - V)}{V(V_0 - V^*)}\right) \tag{18}$$

for P_i and

$$C_{P,conf.} = \frac{U_0 V_0 V^{*2}\alpha_P(V_0 - V)}{V^2(V_0 - V^*)^2}\exp\left(\frac{V^*(V_0 - V)}{V(V_0 - V^*)}\right) \tag{19}$$

for $C_{P,conf.}$ and

$$\text{CED} = \frac{-U_0 V_0(V - V^*)}{V^2(V_0 - V^*)}\exp\left(\frac{V^*(V_0 - V)}{V(V_0 - V^*)}\right) \tag{20}$$

for CED. If we set

$$\left(\frac{\partial P_i}{\partial V}\right)_P$$

equal to zero, the volume V_m at which P_i is equal to maximum, $P_{i,max.}$, is obtained as follows:

$$V_m = \frac{V_0(3V_0 - 4V^*) + V_0\sqrt{8(V_0 - V^*)^2 + V_0^2}}{4(V_0 - V^*)} \tag{21}$$

The relationships between V^*, V_0, U_0, V_m and $P_{i,max.}$ are shown schematically in *Figure 1*.

RESULTS

The values of V^*, V_0, and U_0 used in equations (14), (18)–(21) are determined by equation (18) based on the best fitting with the experimental data of P_i which is given in equation (15), and at atmospheric pressure $P_i \approx \gamma_v T$. The quantities determined are given in *Table 1*, which are used to evaluate $U_{conf.}$, P_i, CED and $C_{P,conf.}$ for polymer and simple liquids in this work. The comparisons of $U_{conf.}$, P_i, and $C_{P,conf.}$ evaluated above with experimental results are shown in *Figures 4–6*, respectively.

The values of α_P and γ_V for polymers are obtained from previous work[15], and those for simple liquids are determined partly from the present work and partly from the literature[1,25]. The typical comparisons of our calculated values of α_P and γ_V for benzene and n-heptane with experimental data given by Rowlinson[1] in the temperature range up to T_C are made, and excellent agreement within 4.0 and 3.8%, respectively, are obtained except near T_C. The α_P and γ_V data for 10 amorphous polymer liquids and 18 simple liquids in the temperature range up to T_C are shown in *Figures 2 and 3*, respectively, where the master curves are obtained and expressed by

$$\ln(\alpha_P T)^{-1} = \alpha_0 + \alpha_1 X \tag{22}$$

$$\ln\frac{\gamma_V V - \gamma_{V_C} V_C}{\gamma_V V} = b_0 + b_1 X + b_2 X^2 \tag{23}$$

where $X = \ln((T_C - T)/T)$, a_0, a_1, b_0, b_1, and b_2 are constants and are given in *Table 2* for individual materials. For polymer liquids, T_C and $\gamma_{V_C} V_C$ are not experimental data and are used only as reduction parameters. The determination of T_C for polymers is based on the master curve of $\ln(\alpha_P T)^{-1}$ against $\ln((T_C - T)/T)$ obtained from simple liquids by assuming that polymer liquids obey the same master curve as the simple liquids. Values of $\ln(\alpha_P T)^{-1}$ for polymers are used to fit the master curve and then determine T_C for polymers. Since T_C determined by different values of $\ln(\alpha_P T)^{-1}$ varies in the range 2–5% for various polymers, the average value of T_C is used to determine the $\ln(\alpha_P T)^{-1}$–$\ln((T_C - T)/T)$ lines for polymers. Similar procedures are used to determine $\gamma_{V_C} V_C$ for polymers. Values of $\gamma_{V_C} V_C$ for simple liquids can be obtained from data in previous work[21], and values of T_C and $\gamma_{V_C} V_C$ for polymers are listed in *Table 2*.

DISCUSSION

The master curves shown in *Figures 2 and 3* indicate that the quantities obey corresponding state theory, in which T_C and $\gamma_{V_C} V_C$ are reduction parameters for $\alpha_P T$ and $\gamma_V V$, respectively, which means that it should have the same quantities of $(\alpha_P T)^{-1}$ and $\{\gamma_V V - \gamma_{V_C} V_C\}/\gamma_V V$ for different polymer and simple liquids if they have the same reduction temperature $(T_C - T)/T$ at atmospheric pressure. In fact, $\alpha_P T$ is usually used to evaluate the reduction temperature T^* from that of a reference liquid in corresponding state theory, because $\alpha_P T$ is a dimensionless quantity or $\alpha_P T = \tilde{\alpha}_P \tilde{T}$[41]. Suppose a liquid has a value of $\alpha_P T$ at temperature T_1, and the reference liquid has the same $\alpha_P T$ at T_r, these two temperature must correspond to the same reduced temperature, i.e.

$$\tilde{T} = \frac{T_1}{T_1^*} = \frac{T_r}{T_r^*} \text{ or } \frac{T_1}{T_r} = \frac{T_1^*}{T_r^*} \tag{24}$$

and from *Figure 2* or equation (22)

$$X = \frac{T_{C,1} - T_1}{T_1} = \frac{T_{C,r} - T_r}{T_r} \text{ or } \frac{T_1}{T_r} = \frac{T_{C,1}}{T_{C,r}} \tag{25}$$

and by equations (24) and (25)

$$\frac{T_{C,1}}{T_{C,r}} = \frac{T_1^*}{T_r^*} \tag{26}$$

Equation (26) shows the starting point of corresponding

Table 1 Parameters used in equations (14), (18)–(21) for various polymer and simple liquids

Material	V^* (cm^3/g)		V_0 (cm^3/g)		$-U_0$ (J/g)			V_m (cm^3/g)	$P_{i,\max.}$ (bar)
	This work	L-J V^* [a]	This work	L-J V_0 [a]	This work	L-J $-U_0$ [a]	U_0 (this work)/ U_0 (L-J)		
Ar[1]	0.3646	0.2884	0.4987	0.4087	185.9	19.42	9.6	0.6176	2015.0
	0.3759[b]		0.5316[b]			149.0[b]		0.6860	2083.8
			0.5657[22]			194.1[22]			
			0.5657[40]			193.9 ± 1.3[40]			
N_2[1]	0.6752	0.6170	0.8890	0.8726	204.2	21.20	9.6	1.0825	1570.2
			0.9643[23]						
O_2[1]	0.4817	0.4110	0.6397	0.5812	219.6	27.72	7.9	0.7819	2231.1
CH_4[1]	1.3751	1.0438	1.8169	1.4761	515.0	77.22	6.7	2.2160	1897.9
CCl_4[1]	0.2896	0.4315	0.3854	0.6102	318.1	17.44	18.2	0.4717	5298.9
n-Heptane[1]	0.8079	0.7941	1.0130	1.1231	387.0	38.15	10.1	1.2036	3563.2
Benzene[1,29]	0.6682	0.6183	0.8270	0.8744	382.6	43.95	8.7	0.9755	4722.7
n-C_6H_{14}[25]	0.8343	0.7724	1.0545	1.0923	390.4	38.61	10.1	1.2583	3272.6
n-C_8H_{18}[25]	0.8631		1.0699		331.1			1.2632	3124.1
n-$C_{16}H_{34}$[25]	0.7309		0.9202		400.6			1.0958	3950.5
n-$C_{22}H_{46}$[25]	0.7779		0.9597		339.3			1.1300	3692.3
Cyclohexane[26,27]	0.8478	0.8875	1.0124	1.2551	283.5	29.41	9.6	1.1691	3743.9
Methyl cyclohexane[28]	0.7833		0.9974		425.1			1.1947	3588.3
CCl_2F_2[30]	0.1187		0.2033		931.6			0.2698	8933.9
$CHClF_2$[30]	0.3774		0.4737		261.1			0.5632	5104.8
CH_3Cl[30]	0.6660	0.4571	0.8225	0.6464	286.4	57.64	5.0	0.9690	3609.9
CH_3Br[30]	0.3583	0.2321	0.4183	0.3282	145.6	39.34	3.7	0.4761	5634.4
CH_3I[30]	0.2277		0.3105		215.9			0.3840	3886.8
CH_3COOCH_3[30]	0.6351	0.5128	0.8285	0.7253	440.6	52.79	8.4	1.0044	3844.8
$CH_3COOC_2H_5$[30]	0.5694	0.5057	0.7501	0.7151	439.6	49.26	8.9	0.9136	3994.2
PS[30]	0.4244		0.6110		634.6			0.7717	4367.8
POMS[30]	0.8295		0.9115		108.0			0.9921	3655.4
PVME[30]	0.8059		0.8982		122.6			0.9887	3535.5
PIB[30]	0.7343		0.8803		247.1			1.0191	3637.4
PMMA[30]	0.5763		0.7545		461.9			0.9163	4330.8
PNBMA[30]	0.7175		0.8294		197.6			0.9375	4220.8
PCHMA[30]	0.7413		0.8307		138.3			0.9180	4050.2
PC[30]	0.5738		0.7183		336.4			0.8528	4416.6
PA[30]	0.6444		0.7504		204.4			0.8526	4509.7
PH[30]	0.5184		0.6857		561.7			0.8367	5449.3

[a] Calculated from Lennard-Jones potentials, detailed procedures are given in text
[b] Calculated from Simha's equation and reduction parameters; see text for detailed procedures

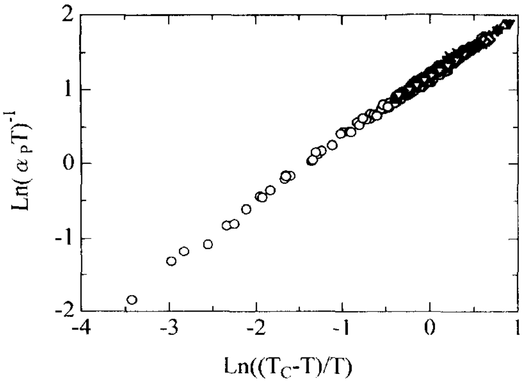

Figure 2 Plot of $\ln(\alpha_P T)^{-1}$ *versus* $\ln((T_C - T)/T)$ for: ○, 128 data of 18 simple liquids including benzene, heptane, argon, nitrogen, oxygen, methane, CCl_4, cyclohexane, methyl cyclohexane, ammonia, CCl_2F_2, $CHClF_2$, CH_3Cl, CH_3I, CH_3Br, C_2H_5Br, CH_3COOCH_3, and $CH_3COOC_2H_5$; ●, PS; □, PCHMA; ■, PC; △, PVME; ▲, POMS; ◇, PNBMA; ◆, PA; ▽, PH; ▼, PIB; ×, PECH

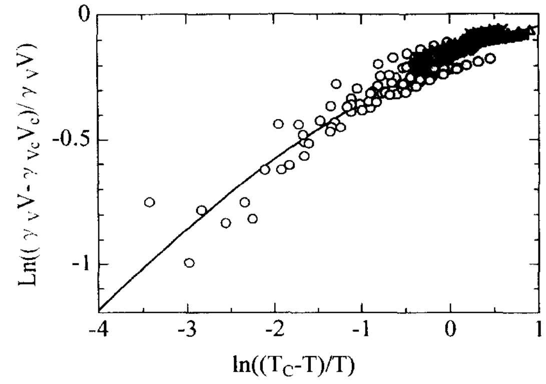

Figure 3 Plot of $\ln((\gamma_V V - \gamma_{V_C} V_C)/\gamma_V V)$ *versus* $\ln((T_C - T)/T)$ for: ○, 118 data of 16 simple liquids including benzene, heptane, argon, nitrogen, oxygen, methane, CCl_4, cyclohexane, methyl cyclohexane, CCl_2F_2, $CHClF_2$, CH_3Cl, CH_3I, C_2H_5Br, CH_3COOCH_3, and $CH_3COOC_2H_5$; ●, PS; □, POMS; ■, PVME; △, PIB; ▲, PNBMA; ◇, PCHMA; ◆, PC; ▽, PA; ▼, PH; ×, PECH

Table 2 Critical values and coefficients used in equations (22) and (23) for various polymer and simple liquids

Material	a_0	a_1	b_0	b_1	b_2	T_C (K)[a]	V_C (cm^3/mol)[a]	γ_{V_C} (bar/K)[a]	k	Ref.
Ar	1.2457	0.8882	−0.2193	0.1205	−0.0471	150.86	74.6	1.8	0.9785	1
N_2	1.2123	0.8588	−0.2051	0.1111	−0.0521	126.1	90.1	1.6	1.2986	1
O_2	1.1786	0.8505	−0.2192	0.1118	−0.0660	154.77	75.0	1.97	0.9408	1
CH_4	1.2416	0.8536	−0.2134	0.1250	−0.0284	190.6	99.0	1.42	1.0935	1
CCl_4	1.1085	0.7192	−0.1399	0.0999	−0.0715	556.35	276.0	0.58	1.3255	1
n-Heptane	1.1948	0.8669	−0.0963	0.1188	−0.0217	540.25	430.0	0.35	1.7241	1
Benzene	1.1159	0.7756	−0.1381	0.1100	−0.0572	562.09	256.0	0.617	1.8937	1,29
Cyclohexane	1.0919	0.5978	−0.1410	0.1694	−0.0093	553.2	308.1	0.592	2.0479	26,27
Methyl cyclohexane	1.1353	0.7655	−0.1337	0.0809	−0.0293	572.1	344.1	0.543		28
NH_3	1.4405	1.1247	−0.5673	−0.2136	−0.0489	405.6	72.5	2.195		30
CCl_2F_2	1.3097	0.9612	−0.1535	0.1801	−0.0021	385.0	217.0	0.75	1.2439	30
$CHClF_2$	1.3224	0.9603	−0.0775	0.2121	0.0014	369.2	165.0	1.002	1.6169	30
CH_3Cl	1.0561	0.6934	−0.2335	0.0181	−0.0839	416.3	139.0	1.13	0.8227	30
CH_3I	1.1579	0.7413	−0.2284	0.1391	−0.0435	528.0	190.0	0.886		30
CH_3Br	1.1494	0.7634				464.0			2.9683	30
CH_3CH_2Br	1.0927	0.6693	−0.1752	0.2085	−0.1274	503.8	215.0	0.797	3.3274	30
CH_3COOCH_3	1.1866	1.0204	−0.1642	0.0680	−0.0412	506.8	228.0	0.758		
Ethyl acetate	1.1251	0.7788	−0.1620	0.1087	−0.0414	523.2	286.0	0.629	0.9205	31
							$\gamma_{V_C} V_C$ (bar cm^3/(g K))			
PS	1.2686	0.6249	−0.0965	0.0655	−0.0152	1065.5	0.5258		0.8339	37
POMS	1.2559	0.6112	−0.1250	0.1355	−0.0836	1049.3	0.6908		2.0863	37
PVME	1.2081	0.7590	−0.1580	0.1696	−0.0950	937.2	0.4006		3.2373	36
PIB	1.2625	0.6943	−0.1382	0.1103	−0.0340	943.3	0.4368		1.2038	33
PNBMA	1.1934	0.7254	−0.1251	0.1081	−0.0539	841.2	1.0197		1.5796	35
PCHMA	1.1803	0.8302	−0.1440	0.1701	−0.1713	947.3	0.9470		1.7775	35
PC	1.1697	0.7990	−0.1549	0.0961	−0.0454	1025.0	1.0684		0.5181	34
PA	1.1925	0.6336	−0.1461	0.1025	−0.0594	1076.3	0.9614		1.3518	34
PH	1.1785	0.7572	−0.1312	0.0825	−0.0200	977.5	1.1517		1.1743	34
PECH	1.3358	0.4727	−0.0921	0.0584	−0.0031	935.4	0.5196		1.4708	38
Master curve	1.1820	0.8425	−0.1724	0.1520	−0.0255				$\bar{k} = 1.5, 598$	

[a] T_C, V_C, and γ_{V_C} for Ar, N_2, O_2, CH_4, CCl_4, *n*-heptane, and benzene are taken from Ref. [1], the values of γ_{V_C} for other materials are calculated based on *Figure 5* of Ref. [21], T_C and V_C for cyclohexane and methyl cyclohexane are taken from Refs [26] and [28], respectively, and for other materials are taken from Ref. [32]

Table 3 Comparison of T^* determined by Flory's method with those by equation (26)

n-Heptane[a]			Benzene[a]				
T (K)	$\alpha_P \times 10^{-3}$	T^* (K)[b]	T (K)	$\alpha_P \times 10^{-3}$	T_1^* (K)[b]	T_2^* (K)[c]	Std.[d]
273.15	1.211	4533	278.67	1.20	4598	4716	2.5
293.15	1.234	4648	293.15	1.22	4675	4836	3.3
313.15	1.29	4710	313.15	1.25	4780	4900	2.5
333.15	1.36	4760	333.15	1.29	4872	4953	1.6
353.15	1.45	4799	353.15	1.35	4939	4993	1.1
373.15	1.58	4811	373.15	1.45	4964	5006	0.8
423.15	2.08	4843	423.15	1.83	5008	5039	0.6
473.15	3.28	4884	473.15	2.60	5055	5081	0.5

[a] T and α_P data are taken from Ref. [1], T_C of *n*-heptane is 540.25 K, of benzene is 562.09 K
[b] Determined by the relationships[6]: $\tilde{T} = (\tilde{V}^{1/3} - 1)/\tilde{V}^{4/3}$, $\tilde{V}^{1/3} - 1 = \alpha_P T/3(1 + \alpha_P T)$
[c] Determined by equation (26) by using *n*-heptane as reference liquid
[d] Std. $= 100 \times (T_2^* - T_1^*)/T_2^*$

state theory, and one can determine the reduction temperature of a liquid from its critical temperature. By selecting *n*-heptane as reference liquid, we have determined T^* of benzene and compared them with those determined by Flory's equation of state in *Table 3*, where good agreements are obtained.

Table 1 gives the comparison of the values of V^*, V_0, and U_0 calculated in this work with those determined by the Lennard-Jones (L-J) potentials, the equation of state and experiments. In the case of the L-J potential, the parameters ε and σ which are determined by second virial coefficients, viscosity and diffusion coefficients in the gas state are taken from previous work[32]. By assuming that molecules have spherical symmetry, then $V^* = (4/3)\pi(\sigma/2)^3 N_0 = \pi N_0 \sigma^3/6$

(cm^3/mol), $V_0 = (4/3)\pi(\sigma_0/2)^3 N_0 = \sqrt{2}\pi N_0 \sigma^3/6$ (cm^3/mol), and $U_0 = \varepsilon N_0$ (J/mol), where $\sigma_0 = \sqrt{2}\sigma$[11] and N_0 is Avogadro's number. On the other hand, a quantum mechanical technique was applied to an Einstein model of a solid by Bernardes[22], and the heat of sublimation (corresponding to the negative of configurational energy at 0 K) and volume of solid argon were calculated at 0 K. Furthermore, with the aid of equation (2), Nanda and Simha[4] derived a corresponding equation of state and the expressions for $U_{\mathrm{conf.}}$ and P_{i}. They used $A = 1.011$, $B = 2.409$ (corresponding to coordination number $Z = 12$, a face-centred cubic lattice model), and obtained the reduction parameters for argon[24] as: $P^* = 3578$ bar, $V^* = 23.18$ cm^3/mol (this V^* is the reduction volume used in Simha's equation of state, not that used in our equation), and $T^* = 709.6$ K. By their expressions for $U_{\mathrm{conf.}}$ and P_{i}, and the determined reduction parameters, V^*, V_0, U_0, V_{m} and $P_{\mathrm{i,max.}}$ are obtained in this work for argon as shown in *Table 1*, and the experimental results of V_0 and U_0 of argon[40] and V_0 of nitrogen[23] are also obtained. As shown in *Table 1*, the good agreements of V^*, V_0 and U_0 for argon calculated in this work with those determined by experiment[22] and by an equation of state[4] are obtained. Our V_0 of nitrogen is consistent also with the experimental result. Comparisons of V^*, V_0, and U_0 calculated in this work with those determined by the L-J potentials as stated above for various materials are also given in *Table 1*, where good agreements are obtained for V_0 and V^*; however, our values of U_0 are about 10 times larger than those calculated by L-J potentials in most cases. It is noted that our value of 185.9 J/g of $-U_0$ is almost the same as 194.1 and 193.9 J/g for argon determined by Bernardes[22] and Dobbs[40] and approximately equals 149.0 J/g determined by Simha's equation. A reason for the difference between U_0 in the L-J potential and in the equation of state is interpreted as follows. In the L-J case, ε represents only one pair of interactions between two molecules[11] in the gas state, and so does U_0 determined from ε. But in the equation of state data for liquids, one molecule can interact with many other molecules around it. In Bernardes', Simha's, and our methods, all of the interactions are considered and hence the values of U_0 are much larger than those of L-J. The ratios of our values of U_0 to those of L-J mean the apparent number of interacting molecules around a centre molecule in the liquid state and may be equivalent to the coordination number Z in Flory's theory, which is usually 8–10 for liquids[11].

Eyring and Hirschfelder assumed a simple van der Waals model for the dependence of configurational energy on volume in equation (4). Flory and coworkers[6,7] have assumed $n = 1$ in the derivation of the equation of state. Simha and coworkers[24] have found n should be 1.85 in order to fit the experimental internal pressure data to the theory. We have also checked the assumption in this work by plotting $\ln(\gamma_V TV)$ against $\ln V$ for polymer and simple liquids and found that the slopes k corresponding to n are in the range 0.8–2.4 with an average of $\bar{k} = 1.560$ as is shown in *Table 2*. In some cases the $\ln(\gamma_V TV)$–$\ln V$ lines are curves in low temperature and have large deviation near T_{C}, which indicates that equation (4) can only be used in a limited temperature or volume range. In fact, if we accept the assumption of $\tilde{U} = -1/\tilde{V}^{-n}$ in equation (4), then $P_{\mathrm{i}} = (\partial U_{\mathrm{conf}}/\partial V)_T = nP^* V^{*1+n}/V^{1+n}$ is a monotonically decreasing function of V, which means that the valid volume range for equation (4) is $V_{\mathrm{m}} \leq V \leq V_{\mathrm{C}}$ in *Figure 1*. In *Figure 4* the values of $U_{\mathrm{conf.}}$ for argon calculated by equation (14) are compared with those calculated by the L-J potential and van der Waals model using $n = 1$ as did Flory. Values of k or n for argon are $k = 0.9785$ and nearly equal to 1. In the case of $n = 1$, $U_{\mathrm{conf.}} = \gamma_V TV$ is used based on Flory's theory[6,7]. *Figure 4* shows that the values of $U_{\mathrm{conf.}}$ calculated in this work are nearly the same as those determined by other models, but the values of $U_{\mathrm{conf.}}$ are much larger than those determined by the L-J model, because U_0 of L-J is much smaller than ours as is shown in *Table 1*. If the same U_0 as ours is used for the L-J function, the curve obtained has a similar form as ours. Simha's results are also compared in *Figure 4*, where good agreements with ours and the van der Waals model are obtained.

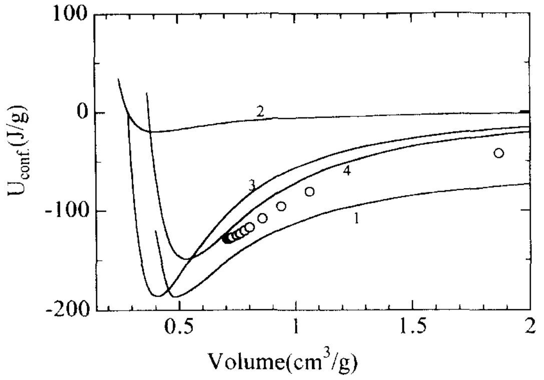

Figure 4 Configurational energy as a function of volume for argon; curve 1, equation (14); curve 2, L-J potential; curve 3, L-J potential with the same U_0 as ours; curve 4, Simha's equation; ○, experimental $\gamma_V TV$

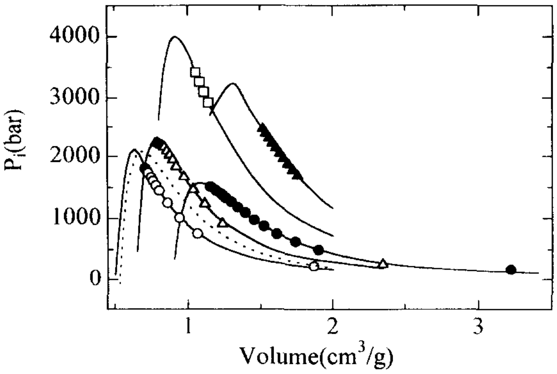

Figure 5 Internal pressure as a function of volume; solid lines are equation (18), dotted line is Simha's equation; points show experimental data. ○, Argon; ●, nitrogen; □, ethyl acetate; △, oxygen; ▲, n-C_6H_{14}

In *Figure 5*, comparison between P_{i} determined by equation (18) and the experimental data up to T_{C} are shown, where excellent agreements are observed. Prigogine and collaborators use equation (2) which is modified from equation (1) to express the dependence of potential on volume and derived the equation of state. Nanda *et al.*[24] evaluated the reduction parameters for argon. Based on their equation and reduction parameters, we have drawn the curve of P_{i} as shown as a dotted line in *Figure 5*, where the agreement is very good except a little difference in V_0 and V_{m}. However, the agreement of P_{i} between experimental data and those values determined by Prigogine's equation of state for n-paraffin is poor, the reason being given by Nanda and Simha[4].

Both Prigogine's and Flory's models can give a general prediction that $C_{\mathrm{P,conf.}}$ increases with temperature and then tends to infinity near T_{C}. In order to examine our equation of

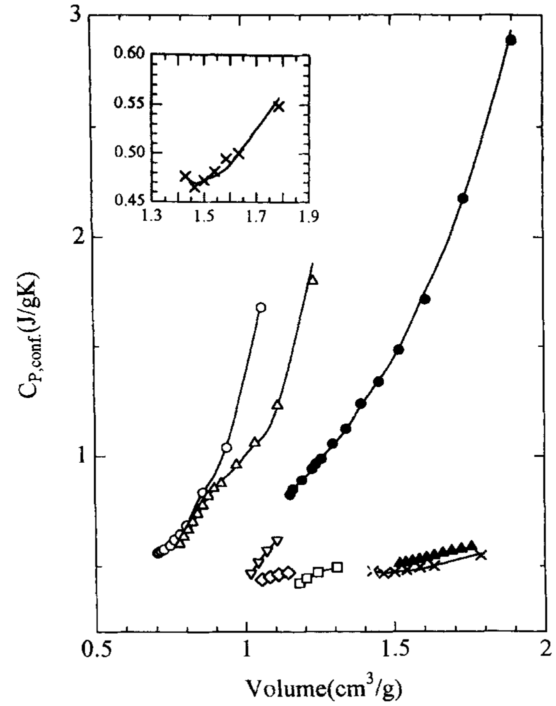

Figure 6 Configurational heat capacity as a function of volume; solid lines are equation (19); points show experimental data. ○, Argon; ●, nitrogen; □, methyl cyclohexane; △, oxygen; ▲, n-C_6H_{14}; ▽, methyl acetate; ◇, ethyl acetate; ×, heptane

$C_{P,conf.}$, we use the following thermodynamic relationship:

$$\gamma_V V \alpha_P T = C_P - C_V \qquad (27)$$

where C_P and C_V are heat capacity at constant pressure and volume, respectively. In the smoothed potential models, the cell partition function depends only on volume and the configurational energy is independent of T at constant volume, thus C_V is zero[3,14], so that the configurational heat capacity is

$$C_{P,conf.} = \gamma_V V \alpha_P T \qquad (28)$$

which can be evaluated easily with aid of our $\alpha_P T$ and $\gamma_V V$ data determined above. The comparison between $C_{P,conf.}$ calculated by equation (19) and experimental results by equation (28) are given in *Figure 6*, where the agreements are quite good. Our model predicts that the configurational heat capacity rises with temperature from a zero value at 0 K, and then increases slowly and becomes infinite in the vicinity of T_C because α_P tends to infinity at T_C. For some organic liquids[39] $C_{P,conf.}$ has a minimum near room temperature. Rowlinson[1] associates it with non-spherical force fields around these molecules. For heptane as an example, equation (19) predicts a minimum $C_{P,conf.} = 0.4699$ J/(g K) at $V = 1.4630$ cm^3/g, where the experimental results show also a minimum $C_{P,conf.} = 0.4658$ J/(g K), but both Prigogine's and Flory's models predict only a monotonically increasing tendency of $C_{P,conf.}$ with temperature.

CONCLUSIONS

We have proposed the empirical equations of configurational energy, configurational heat capacity, internal pressure, and cohesive energy density. The parameters used in the above equations, i.e. V^*, V_0, and U_0, are determined for various materials including polymer and simple liquids which are useful to evaluate $U_{conf.}$, P_i, CED and $C_{P,conf.}$. The comparisons between our calculated and literature values of V_0, V^* and U_0 are made. The agreements of V_0 and V^* with the corresponding L-J parameters are good, but U_0 is about 10 times of that of L-J in most cases. It is suggested that the ratios of our U_0 values to those of L-J correspond to the coordinate number Z in Flory's theory. The comparisons of $U_{conf.}$, P_i, and $C_{P,conf.}$ determined in this work with those determined by the models of L-J and van der Waals model are made and good agreements are observed for them except for $U_{conf.}$ in the case of the L-J potential because of the difference of U_0. Especially, equation (19) can predict the minimum of $C_{P,conf.}$ at room temperature for heptane.

The empirical expressions of $\alpha_P T$ and $\gamma_V V$ are also derived in this work which indicate these quantities obey corresponding state theory. By using equation (26), one can determine the reduction parameter of a liquid from its critical temperature.

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