

Semiempirical examination of the van der Waals and Tonks models for polymers and simple liquids

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Semiempirical examination of the van der Waals and Tonks models for polystyrene and polyisobutylene polymers and the simple liquids n-heptane, benzene and carbon tetrachloride has been done using an empirical equation derived from the thermodynamic equation of state and experimental data for the thermal pressure coefficient γ_v , molar volume V and heat capacity C_v at constant volume. The equation derived for internal energy is expressed as $E = (\gamma_v T - P)(V - V_0) + 3RT/2$ and is found to be useful in determining the internal energy of polymers and simple liquids, where V_0 is a constant volume. The internal energy function has strong correlations with internal energy for the van der Waals model and with entropy for the Tonks model. It is discussed through comparisons of our internal energy function with other models whether the van der Waals and Tonks models are the best ones to use or not.

(Keywords: van der Waals model; Tonks model; thermodynamic equation of state; internal energy)

INTRODUCTION

It has been recognized that the main thermodynamic properties of polymer solutions, such as phase separation, are explained through differences in thermal pressure coefficient and thermal expansion coefficient between the polymer and the simple liquid solvent. The universal equation of state or the reduced equation of state for the polymer and the simple liquid is essential to evaluate these differences¹. Extensive studies on the equation of state for polymers and simple liquids have been made by Prigogine *et al.*², Flory *et al.*³, Simha *et al.*⁴ and Patterson *et al.*⁵ Flory *et al.*³ have derived the reduced equation of state using the van der Waals model for the internal energy and the Tonks model⁶ for the entropy in the liquid state. They have explained theoretically the upper and lower critical solution temperatures in polymer solutions through differences in equation-of-state parameters between polymer and solvent. The corresponding-states theories of Flory *et al.* and Patterson *et al.*⁷ based on the Prigogine theory⁸ have successfully predicted other thermodynamic properties of polymer solutions, such as the pressure dependence of the upper and lower critical solution temperatures^{9,10}, the concentration dependence of the χ parameter¹¹ and the excess volume of mixing¹². However, it is also found that the prediction of the corresponding-states theory is qualitative or semi-quantitative in most cases and empirical adjustable parameters or a temperature shift is needed to fit with the experimental values¹³. Improvements of the theory have been made from the viewpoint of the van der Waals model¹⁴, the random mixing approximation^{15,16}, the effect of orientational order¹⁷ and the lattice fluid theory¹⁸.

In this work we have tried to examine semiempirically the van der Waals model for the internal energy and the Tonks model for the entropy used in the Flory theory of corresponding states with the aid of the thermodynamic equation of state and experimental data for the thermal pressure coefficient γ_v , molar volume V and heat capacity C_v at constant volume. In this work we selected two typical polymers, polystyrene and polyisobutylene, and three simple liquids, n-heptane, benzene and carbon tetrachloride, to obtain useful information on the universal equation of states for polymers and simple liquids.

DERIVATION OF THE INTERNAL ENERGY FUNCTION FOR POLYMERS AND SIMPLE LIQUIDS

Calculation of the internal energy E for polymers and simple liquids has been carried out on the basis of the thermodynamic equation of state given by

$$(\partial E / \partial V)_T = \gamma_v T - P \quad (1)$$

We assumed that the function E is simply expressed by

$$E = (\gamma_v T - P)f(V) + 3RT/2 \quad (2)$$

where R is the gas constant. The function $f(V)$ is given by

$$f(V) = V - V_0 \quad (3)$$

and the following equation is also obtained (see Appendix I):

$$\gamma_v T - P = g(T) \quad (4)$$

where V_0 in equation (3) is a constant volume and $g(T)$ in equation (4) expresses a function of temperature. The internal energy E is given from equations (2) and (3) by

$$E = (\gamma_v T - P)(V - V_0) + 3RT/2 \quad (5)$$

Values of V_0 are calculated from the temperature derivative of equation (5) at constant pressure (see Appendix II):

$$(\partial E / \partial T)_v = (\partial(\gamma_v T - P) / \partial T)_p (V - V_0) + 3R/2 \quad (6)$$

or

$$V_0 = V - (C_v - 3R/2) / (\partial \gamma_v T / \partial T)_p \quad (7)$$

where $C_v = (\partial E / \partial T)_v$ is the heat capacity at constant volume. One can say that the equation (6) is equivalent to

$$(\partial E / \partial T)_v = 3R/2 + (\partial(\gamma_v T - P) / \partial T)_v (V - V_0)$$

because of $(\gamma_v T - P) = g(T)$ in equation (4).

RESULTS OF CALCULATIONS AND DISCUSSIONS

All experimental data for the thermal pressure coefficient γ_v , molar volume V and heat capacity at constant volume C_v for the simple liquids n-heptane, benzene and carbon tetrachloride used in the calculations are obtained from the literature¹⁹, while data for γ_v and molar volume per monomer unit V_m for polymers are from data for polystyrene²⁰ and polyisobutylene²¹. Values of C_v for polymers are obtained from values of C_p for these

Table 1 Constant values of a and b in equation (8) for polymers and simple liquids

	$a \times 10^2$ (bar K ⁻²)	$b \times 10^{-3}$ (bar)
Polystyrene	-1.13	5.16
Polyisobutylene	-0.598	3.90
n-Heptane	-1.16	3.58
Benzene	-1.49	4.98
Carbon tetrachloride	-1.76	4.95

Table 2 Values of V_0 calculated by equation (7) for polymers and simple liquids

Temperature (°C)	V_0 (cm ³ mol ⁻¹)				
	Polystyrene	Polyisobutylene	n-Heptane	Benzene	Carbon tetrachloride
-20					179
0	317	307	389	182 ^a	175
20			387	182	173
25	309	304			
40			385	183	171
50	303	303			
60			385	186	170
80			385	188	
100	280	301	388		
150		299	399		
200			420		
250			479		

^a Value at 5.524°C

polymers²² and the thermodynamic equation

$$C_v = C_p - \gamma_v V T \alpha_p$$

where α_p is the thermal expansion coefficient at constant pressure. Values of $(\partial \gamma_v T / \partial T)_p$ in equation (7) are calculated using an empirical equation for $\gamma_v T$ such as

$$\gamma_v T = aT^2 + b \quad (8)$$

where a and b are constants. Values of $\gamma_v T$ calculated by equation (8) agreed with the experimental values within 3% over the temperature range 0–200°C for n-heptane and benzene and –23 to 70°C for carbon tetrachloride, and within 2% over 0–100°C for polystyrene and 0–150°C for polyisobutylene. Values of a and b in equation (8) for these simple liquids and polymers are given in Table 1. Values of V_0 calculated by equations (7) and (8) are given in Table 2, where values of V_0 are almost constant over the wide temperature range.

A semiempirical equation of state derived from equation (5) is expressed by

$$PV/T = \gamma_v V - (E - 3RT/2)V/T(V - V_0) \quad (9)$$

Verifications that equation (9) is derived from statistical thermodynamics are shown in Appendix III, where it is also shown that the left-hand side of equation (9) is equal to the right-hand side in the case of an ideal gas. The examination of the van der Waals and Tonks models has been carried out using equation (9). The internal energy and equation of state for the van der Waals model are given by

$$E_{vdw} = -a_0/V \quad (10)$$

and

$$PV/T = VR/(V - b_0) - a_0/VT \quad (11)$$

where a_0 and b_0 are constants and R is the gas constant. The following correspondence between the terms in equations (11) and (9) is obtained:

$$VR/(V - b_0) \leftrightarrow \gamma_v V$$

and

$$E_{vdw} \leftrightarrow -(E - 3RT/2)V/(V - V_0)$$

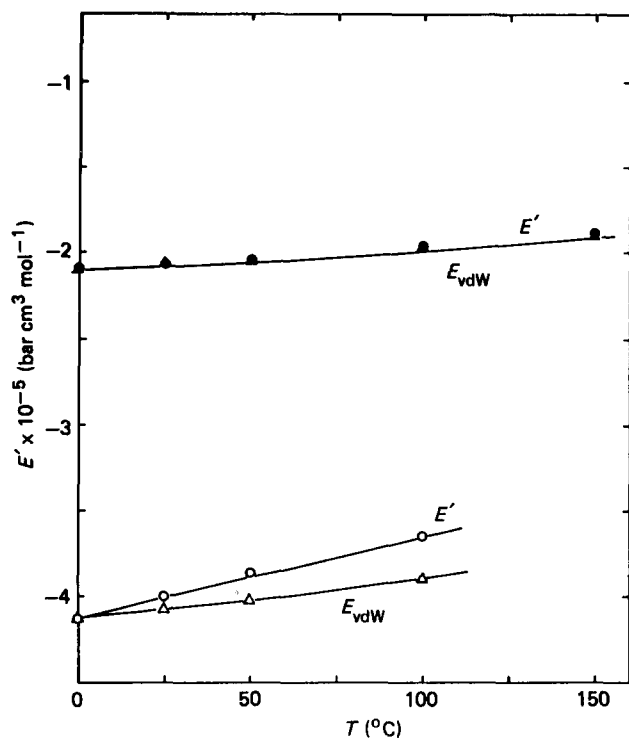


Figure 1 Temperature dependence of the internal energy E' (○, ●) in equation (12) and E_{vdW} (△, ▲) in equation (10) for polystyrene (○, △) and polyisobutylene (●, ▲)

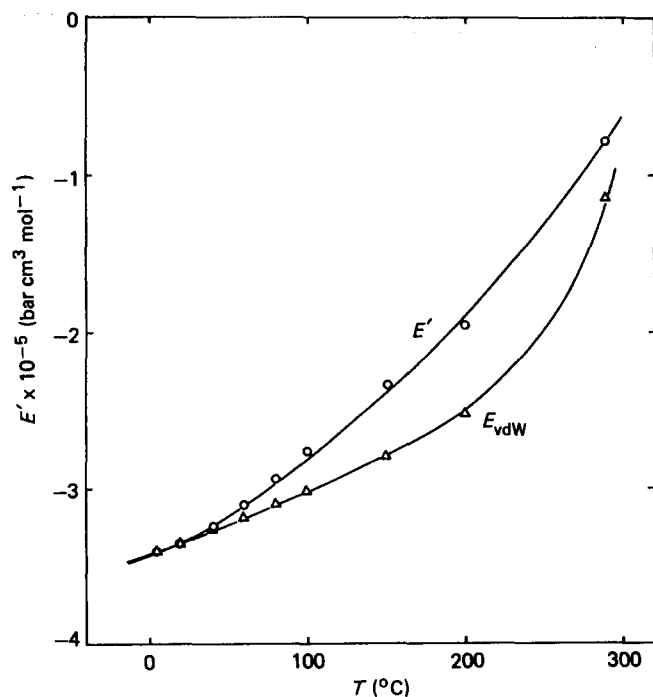


Figure 2 Temperature dependence of the internal energy E' (○) in equation (12) and E_{vdW} (△) in equation (10) for benzene

where $-(E - 3RT/2)V/(V - V_0)$ is expressed using equation (5) by

$$-(E - 3RT/2)V/(V - V_0) = -(\gamma_v T - P)V = E' \quad (12)$$

It is noteworthy that the function E_{vdW} is not equal to E in equation (5) and equal to E' defined by equation (12). Comparisons between the function E_{vdW} and E' are shown

in Figures 1, 2 and 3, where values of a_0 are determined by fitting the values of equation (10) with that of equation (12) at room temperature. Deviations between the two functions are considerable over the high-temperature range, except for polyisobutylene.

Flory *et al.*^{1,3} have derived the reduced equation of state using the Tonks model for the entropy and the van der Waals model for the internal energy, which is given by

$$\tilde{P}\tilde{V}/\tilde{T} = \tilde{V}^{1/3}/(\tilde{V}^{1/3} - 1) - (\tilde{V}\tilde{T})^{-1} \quad (13)$$

where the reduced variables $\tilde{P} = P/P^*$, $\tilde{V} = V/V^*$ and $\tilde{T} = T/T^*$ are calculated from the actual values of P , V and T and the reduction parameters P^* , V^* and T^* . The term $\tilde{V}^{1/3}/(\tilde{V}^{1/3} - 1)$ calculated by the Tonks model reflects the entropy contribution to the compressibility factor, while the last term $(\tilde{V}\tilde{T})^{-1}$ in equation (13) is due to the internal energy. It is proved from statistical thermodynamics that the term $\tilde{V}^{1/3}/(\tilde{V}^{1/3} - 1)$ is essentially the same as the quantity $\gamma_v V = (\partial S/\partial V)_T V$ if the Tonks model $\Omega \propto (V^{1/3} - V^{*1/3})^3 N$ is used, where Ω is the total free volume and N is the number of molecules. It is also proved that the internal energy term $(\tilde{V}\tilde{T})^{-1}$ in equation (13) is essentially the same as the quantity E'/T in equation (9). The proof based on statistical thermodynamics is given in Appendix III.

Comparisons of the entropy terms $RV/(V - b_0)$ in equation (11), $\tilde{V}^{1/3}/(\tilde{V}^{1/3} - 1)$ in equation (13) and $\gamma_v V$ in equation (9) are given in Figures 4, 5 and 6. The actual values of the entropy term in equation (13) are calculated from $c_1 R \tilde{V}^{1/3}/(\tilde{V}^{1/3} - 1)$, where $3c_1$ is the number of external degrees of freedom of the molecule³. Values of V^* for n-heptane, benzene and carbon tetrachloride are calculated using equation (13) at $P = 0$ and experimental

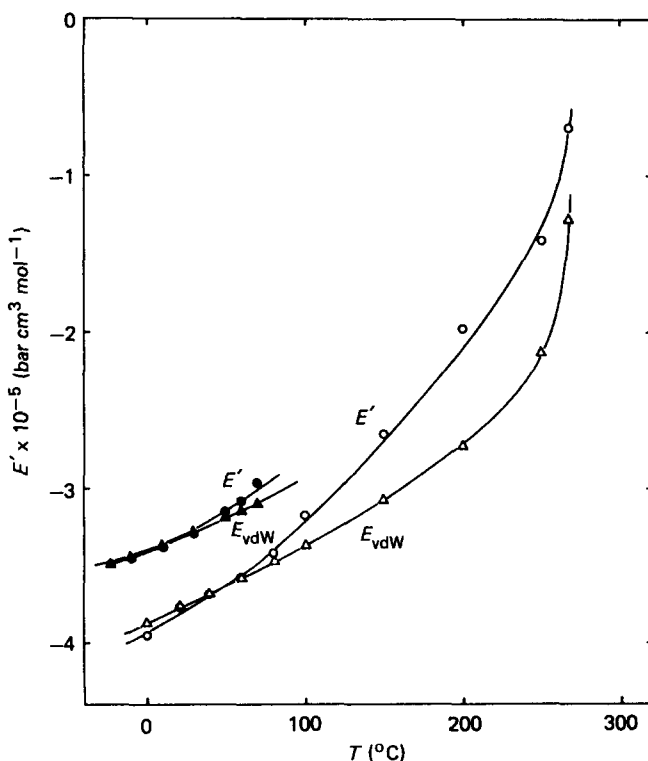


Figure 3 Temperature dependence of the internal energy E' (○, ●) in equation (12) and E_{vdW} (△, ▲) in equation (10) for carbon tetrachloride (●, ▲) and n-heptane (○, △)

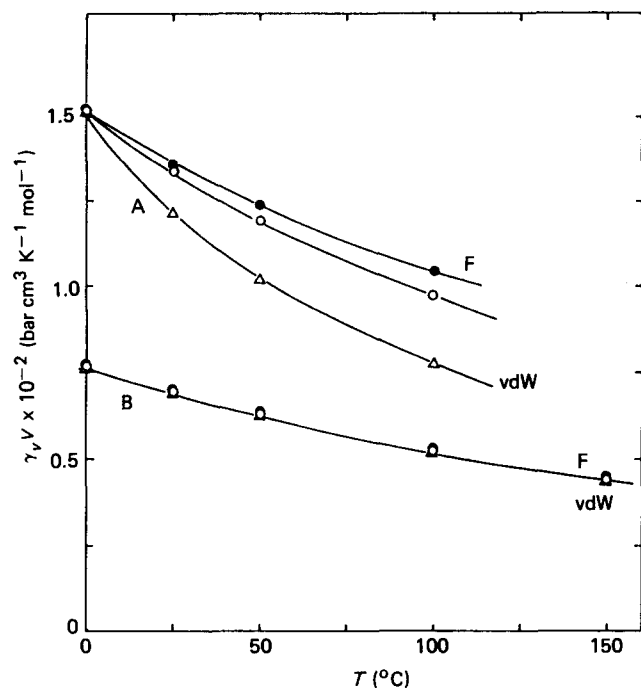


Figure 4 Temperature dependence of $\gamma_v V$ (\circ) and $VR/(V-b_0)$ (\triangle) in equation (11) and $c_1 R \bar{V}^{1/3}/(\bar{V}^{1/3}-1)$ (\bullet) in equation (13) for polystyrene (A) and polyisobutylene (B)

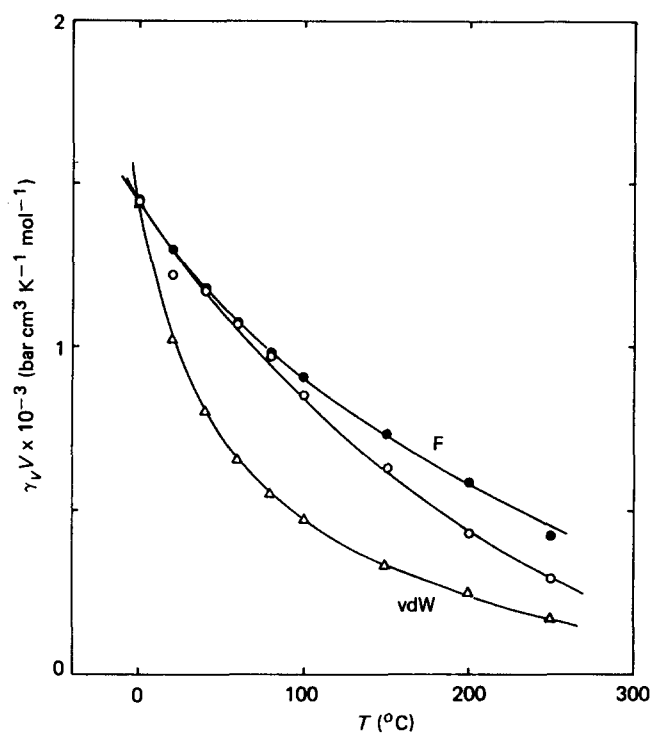


Figure 5 Temperature dependence of $\gamma_v V$ (\circ) and $VR/(V-b_0)$ (\triangle) in equation (11) and $c_1 R \bar{V}^{1/3}/(\bar{V}^{1/3}-1)$ (\bullet) in equation (13) for n-heptane

values of the thermal expansion coefficient³, while V^* values per monomer unit for the polymers are taken from the literature for polystyrene²⁰ and polyisobutylene²¹.

The constant values of b_0 in equation (11) and c_1 mentioned above are determined by fitting the value of $\gamma_v V$ with the corresponding terms in equations (11) and (13) at room temperature. It is shown in Figures 4, 5 and 6 that the entropy term $\gamma_v V$ in equation (9) is more similar to that for the Tonks model than to that for the van der Waals model, while large deviations occur between the Tonks model and the term $\gamma_v V$ over the high-temperature range, except for polyisobutylene. The values of a_0 , b_0 , V^* and c_1 used in this work are listed in Table 3, where it is shown that the values of c_1 and a_0 for polyisobutylene are much smaller than those for the other polymer and the simple liquids. It is suggested from these comparisons of our semiempirical equation given by equation (9) with the van der Waals and Tonks models that there are better models for the internal energy and entropy in the liquid state of polymers and simple liquids than the van der Waals and Tonks models.

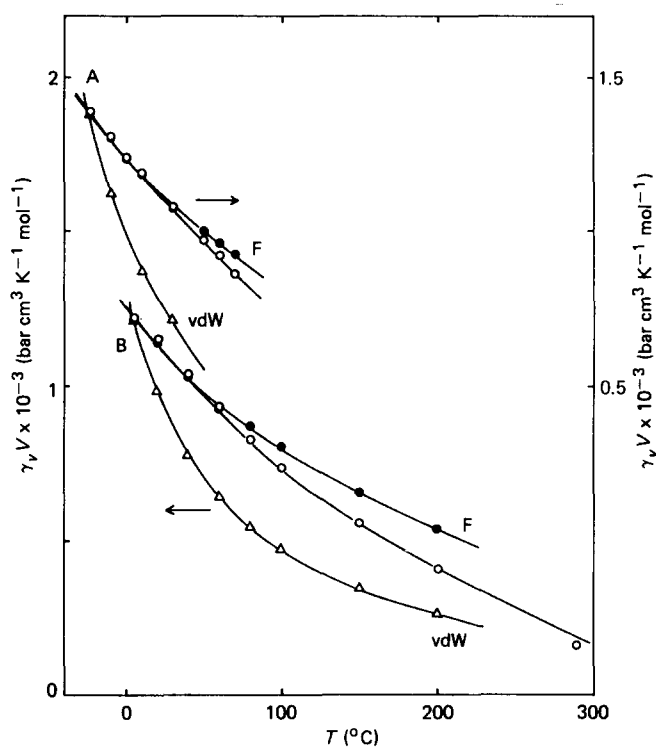


Figure 6 Temperature dependence of $\gamma_v V$ (\circ) and $VR/(V-b_0)$ (\triangle) in equation (11) and $c_1 R \bar{V}^{1/3}/(\bar{V}^{1/3}-1)$ (\bullet) in equation (13) for carbon tetrachloride (A) and benzene (B)

Table 3 Values of a_0 and b_0 in equation (11) and c_1 and V^* in equation (13) used in calculations for polymers and simple liquids

	$a_0 \times 10^{-7}$ (bar cm ⁶ mol ⁻¹)	b_0 (cm ³ mol ⁻¹)	c_1	V^* (cm ³ mol ⁻¹)
Polystyrene	3.96	90.5	0.737 ^a	85 ^a
Polyisobutylene	1.26	53.8	0.364 ^a	53 ^a
n-Heptane	5.52	134.7	1.21	115
Benzene	2.98	81.4	1.04	70
Carbon tetrachloride	3.19	86.2	1.15	74

^a Values per monomer unit of M_u : $M_u = 104.1 \text{ g mol}^{-1}$ for polystyrene and $M_u = 56.1 \text{ g mol}^{-1}$ for polyisobutylene

APPENDIX I

Derivation of equations (3) and (4)

From the volume derivative of equation (2) at constant temperature, it is given that

$$(\partial E/\partial V)_T = (\partial(\gamma_v T - P)/\partial V)_T f(V) + (\gamma_v T - P)(\partial f(V)/\partial V)_T \quad (\text{A.I.1})$$

From comparison between equation (A.I.1) and equation (1), it is obtained that

$$(\partial f(V)/\partial V)_T = 1 \quad (\text{A.I.2})$$

and

$$(\partial(\gamma_v T - P)/\partial V)_T = 0 \quad (\text{A.I.3})$$

From equations (A.I.2) and (A.I.3), the function $f(V)$ is given by

$$f(V) = V - V_0 \quad (\text{A.I.4})$$

and

$$(\gamma_v T - P) = g(T) \quad (\text{A.I.5})$$

where V_0 is a constant and $g(T)$ means a function of temperature.

APPENDIX II

Derivation of equation (6)

From the temperature derivative of equation (5) at constant pressure, it is given that

$$(\partial E/\partial T)_P = (\partial(\gamma_v T - P)/\partial T)_P (V - V_0) + (\gamma_v T - P)(\partial V/\partial T)_P + 3R/2 \quad (\text{A.II.1})$$

On the other hand, the heat capacity at constant pressure C_p is related to $(\partial E/\partial T)_P$ through

$$C_p = (\partial(E + PV)/\partial T)_P = (\partial E/\partial T)_P + P(\partial V/\partial T)_P \quad (\text{A.II.2})$$

It is obtained from equations (A.II.1) and (A.II.2) that

$$C_p = (\partial(\gamma_v T)/\partial T)_P (V - V_0) + \gamma_v TV\alpha_p + 3R/2 \quad (\text{A.II.3})$$

or by using the relation that $C_p - C_v = \gamma_v VT\alpha_p$

$$C_v = (\partial(\gamma_v T)/\partial T)_P (V - V_0) + 3R/2 \quad (\text{A.II.4})$$

where $\alpha_p = V^{-1}(\partial V/\partial T)_P$.

APPENDIX III

Derivation of equation (9) from statistical thermodynamics

Following Prigogine² and Flory³, we assume the partition function to take the form

$$Z = (2\pi mkT/h^2)^{3N/2} Z_{\text{comb}} \Omega \exp(-E_0/kT) \quad (\text{A.III.1})$$

where Z_{comb} is a combinatorial factor in which the communal entropy factor may be included, Ω is related to the total free volume available to the system and E_0 is the mean intermolecular energy of the system. From equation (A.III.1), the Helmholtz free energy F is given by

$$F = -kT[\frac{3}{2}N \ln(2\pi mkT/h^2) + \ln(Z_{\text{comb}} \Omega) - E_0/kT] \quad (\text{A.III.2})$$

and the equation of state is given by

$$P = -(\partial F/\partial V)_T = kT[(\partial \ln(Z_{\text{comb}} \Omega)/\partial V)_T - (\partial E_0/\partial V)_T/kT] \quad (\text{A.III.3})$$

If it is assumed that E_0 is a function of volume, the entropy S is expressed by

$$S = k[(3N/2) \ln(2\pi mkT/h^2) + (3N/2) + \ln(Z_{\text{comb}} \Omega)] - (\partial E_0/\partial T)_v \quad (\text{A.III.4})$$

The equation (A.III.3) is recast using equation (A.III.4) to

$$P = (\partial S/\partial V)_T T - (\partial E_0/\partial V)_T \quad (\text{A.III.5})$$

or using the assumption $E_0 = E - \frac{3}{2}RT$ (the internal energy)

$$PV/T = \gamma_v V - (\gamma_v T - P)V/T \quad (\text{A.III.6})$$

$$= \gamma_v V - (E - 3RT/2)V/T(V - V_0) \quad (\text{A.III.7})$$

where the relations $\gamma_v = (\partial S/\partial V)_T$ and $(\partial E/\partial V)_T = \gamma_v T - P$ are used in deriving equation (A.III.6).

In the case of an ideal gas, the left-hand side of equation (A.III.7) is equal to the right-hand side because $E_{\text{ideal gas}} = 3RT/2$ and $\gamma_v = R/V$, and the equation derived is

$$PV/T = R \quad (\text{A.III.8})$$

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