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RIGOROUS AND SIMPLIFIED LATTICE-HOLE EQUATIONS OF STATE FOR CALCULATING SPECIFIC VOLUMES OF COMMON PURE POLYMERS

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Abstract – Specific volumes of common pure polymers such as low- and high-density poly(ethylene), poly(n-butyl methacrylate), poly(styrene), and poly(o-methylstyrene) were calculated by the NLF and the MF-NLF equations of state, which were developed from nonrandom lattice-hole theory. Both models contain only two molecular parameters for a pure r-mer. The NLF model is based on the rigorous approximation of lattice-hole theory and thus it is somewhat complicated in practice. The MF-NLF model is based on the two-fluid approximation of the same lattice-hole theory and thus is relatively more semi-empirical than the NLF, while preserving comparable accuracy. In this work the models were comparatively applied to the calculation of the specific volumes of pure polymers, and the results obtained to date were presented with emphasis on the practical utility of the models.

Key words: Specific Volumes, LDPE, HDPE, PnBMA, PS, Poly(orthomethylstyrene), Lattice Theory, Equations of State

INTRODUCTION

The influence of equation-of-state (EOS) properties on the thermodynamic behavior of polymer systems has received a great deal of attention over the past few decades. As a result, considerable effort has been made to date towards the refinement of statistical-mechanical theories of polymeric fluids. The nearest-neighbor lattice statistical-mechanical theory of Guggenheim [1952] and the cell theory of Prigogine et al. [1957] had a great impact, theoretically and experimentally, on thermodynamic research related to polymer systems. Since then, many EOS theories of polymeric fluids have been proposed.

Some well-known EOSs stem from cell theory [Simha and Somcynsky, 1969, 1971; Flory, 1965; Beret and Prausnitz, 1975; Nies and Stroeks, 1990; etc.]. However a cell-model type partition function requires a separation of internal and external degrees of freedom. External degrees of freedom attributable to a segment of a polymer chain are less than for a similar small molecule. For example, Prigogine et al. [1957] introduced a new parameter 'c' to characterize the decrease in the external degrees of freedom. On the other hand, since the lattice fluid (Ising) theory [Guggenheim, 1952] is not based on a cell concept, the question of how external and internal degrees of freedom are separated is not necessarily encountered, and the introduction of a 'c' parameter is not required.

After the pioneering work of Sanchez and Lacombe [1977, 1978] on the EOS for the Ising fluid, many EOSs originating from lattice fluid theory have also been proposed [Okada and Nose, 1981; Panayiotou and Vera, 1982; Kumar et al., 1987; Smirnova and Victorov, 1987; etc.]. In the previous papers [You et al., 1993, 1994a, b; Yoo et al., 1995a, b, c], the present authors briefly reviewed the existing Ising theories after Guggenheim [1952].

Recently, a new rigorous EOS based on the nonrandom lattice-fluid theory (called 'NLF') and its simplification by a multi fluid-nonrandom lattice fluid theory (called 'MF-NLF') of pure fluids and their solutions have been formulated by the present authors [You et al., 1993, 1994a, b; Yoo et al., 1995a, b, c; Lee and Yoo, 1997]. These two theories require only two EOS parameters for each pure component and one binary parameter for a mixture. Our general objective in the present paper is to survey the applicability of the NLF and the MF-NLF theory to volumetric properties of pure polymers.

EOS PROPERTIES FOR PURE POLYMERS

1. NLF-EOS Theory

As we have discussed elsewhere [You et al., 1993, 1994a, b; Yoo et al., 1995a, b, c], the equation of state based on the approximate nonrandom lattice hole theory for pure component is as follows:

$$P=\left(\frac{1}{V_H\,\beta}\right)\left\{\frac{z}{2}\ln\left[1+\left(\frac{q_1}{r_1}-1\right)\rho-\ln(1-\rho)\right]\right\}-\left(\frac{z\varepsilon_P}{2V_H}\right)\theta_1^2 \tag{1}$$

where

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$$\varepsilon_P = \varepsilon_{11}\left[1 - \left(\frac{\beta\varepsilon_{11}}{2}\right)\theta_0(2\theta_1 - \theta_0)\right] \tag{2}$$

$$\rho = \frac{V_1^*}{V} = \frac{N_A V_H r_1}{V} \tag{3}$$

$$\theta_1 = \frac{(q_1/r_1)\rho}{1 + \rho(q_1/r_1 - 1)} \tag{4}$$

$$\theta_0 = 1 - \theta_1 \tag{5}$$

$$zq_1 = zr_1 - 2r_1 + 2 \tag{6}$$

β=1/kT and N_A is Avogadro's number; r_1 is the segment number of an r-mer and q_1 is the segment surface area parameter. Between these two parameters the relation given in Eq. (6) can be used for open chain r-mers. We set the coordination number z=10 and the unit cell volume V_H=9.75 $cm^3 mol^{-1}$ [You et al., 1994a]. Thus, for a pure fluid we need to determine only two independent molecular parameters, V_1^* and ε_{11}. In the case of polymers, V_1^* is relatively insensitive with respect to temperature. However, ε_{11} is in general a function of temperature; it was regressed at each isotherm and made a simple function of temperature in practice. It is

$$\frac{\varepsilon_{11}}{k} = E_a + E_b(T - T_0) \tag{8}$$

where T_0 is a reference temperature that is arbitrarily set as 298.15 K. Other expressions such as fugacity coefficients, molar configurational internal energy, and second order thermodynamic functions (i.e., the thermal expansion coefficient α_1, the isothermal compressibility coefficient β_1 etc.) are given elsewhere [You et al., 1993, 1994a, b].

Although the NLF-EOS applicable for pure components given above looks simple, it becomes significantly complicated for the extension to multicomponent systems since it was based on the multidimensional series expansion of the configurational Helmholtz free energy of nonrandom lattice-hole theory [You et al., 1994a, b].

2. MF-NLF-EOS Theory

As discussed elsewhere [Yoo et al., 1995; Lee and Yoo, 1997], to simplify the NLF-EOS given above, the present authors introduced the concept of the two-fluid approximation with respect to the nonrandom lattice and hole contribution of the original NLF-EOS. The expression of the MF-NLF-EOS is

$$P = \left(\frac{1}{V_H\beta}\left\{\frac{z}{2}\ln\left[1 + \left(\frac{q_1}{r_1} - 1\right)\rho\right] - \ln(1-\rho)\right\}\right.$$
$$\left. - \frac{z\theta_1^2}{2V_H\beta}\left(\frac{1 - \tau_{01}}{\theta_0\tau_{01} + \theta_1}\right)\right) \tag{9}$$

where

$$\tau_{01} = \exp[\beta(\varepsilon_{11} - \varepsilon_{01})] \tag{10}$$

For pure fluids we set ε_{01}=0. This EOS can be regarded as a simplified version of the previous NLF theory and the definition of the variables is identical with that of the NLF. Thus, this EOS still contains only two pure molecular parameters, V_1^* and ε_{11}, for a pure system. For ε_{11}, the temperature-dependent formular given by Eq. (8) was used.

These two EOSs are readily expandable to multicomponent systems with the introduction of a binary interaction parameter. In this paper, we omit those detailed expressions of the thermodynamic functions of the two models for general mixture systems [You et al., 1994a, b; Lee and Yoo, 1997].

DATA REDUCTION

To evaluate comparatively the utility of the NLF and MF-NLF models in the calculation of volumetric properties of pure polymeric substances, we arbitrarily selected five common polymers: high density poly(ethylene, HDPE) [Hellwege et al., 1961; Rodgers, 1993], low density poly(ethylene, LDPE) [Hellwege et al., 1961; Rodgers, 1993], poly(n-butyl methacrylate, PnBMA) [Olabisi and Simha, 1975], poly (styrene, PS) [Quach and Simha, 1971], poly(o-methyl polystyrene) [Quach and Simha, 1971].

In applying the EOSs to polymer systems, we estimated the molecular parameters, V_1^* and ε_{11}, from the experimental P-ρ-T data by the numerical bisection method [Press et al., 1992]. In the regression, the initial estimates of ε_{11} were provided by a value around 100, and V_1^* was given by a value of 0.7 times the molecular weight of a candidate polymer in general. The best fitted EOS parameters, V_1^* and ε_{11}, for each pure polymer for the NLF-EOS and MF-NLF-EOS with absolute average error deviations are summarized in Tables 1 and 2, respectively.

Table 1. The energy and volume parameters for the NLF model†

Polymer	E_a K	E_b –	V_1^* cm^3/g	AAD (%)
High-density polyethylene	124.49832	.05120	1.09963	.469
Low-density polystyrene	115.18157	.10513	1.09445	.309
PnBMA	118.11379	.10507	.88553	.577
Polystyrene	130.90941	.08278	.88600	.283
Poly(orthomethylstyrene)	139.32543	.05208	.90828	.223

†V_1^* =the temperature independent specific volumes

AAD=1/(number of data) $\Sigma(|volume_{exp} - volume_{cal}|/volume_{exp} \times 100)$

Table 2. The energy and volume parameters for the MF-NLF model†

Polymer	E_a K	E_b –	V_1^* cm^3/g	AAD (%)
High-density polystyrene	133.80667	.012020	1.08668	.424
Low-density polystyrene	122.46545	.08800	1.08501	.267
PnBMA	132.09898	.04216	.88036	.419
Polystyrene	146.18205	.03096	.87741	.247
Poly(orthomethylstyrene)	160.63812	–.03558	.89826	.228

RESULTS AND DISCUSSION

Experimental and calculated specific volumes of high-density poly(ethylene, HDPE) [Hellwege et al., 1961; Rodgers, 1993] at various temperatures and pressures by the NLF and the MF-NLF are shown in Fig. 1. Although the formulation of the NLF is self-consistent with a sound theoretical basis, a less complicated model would be more convenient in engineering-oriented phase equilibrium calculations. Thus, with this background in mind, we developed the MF-NLF model while preserving comparable accuracy with respect to the NL-F. As can be seen from Tables 1 and 2, the overall AAD by the NLF was found to be 0.464, whereas it was 0.424 for the case of MF-NLF. Both models showed reasonably comparable accuracy although the predicting capacity of the MF-NLF was slightly better than that of the NLF. In Fig. 2, a similar comparison of both models is shown for the experimental specific volumes of the low-density poly(ethylene, LD-PE) [Hellwege et al., 1961; Rodgers, 1993]. Again the AAD was 0.309 for the case of the NLF and 0.267 for the case of the MF-NLF.

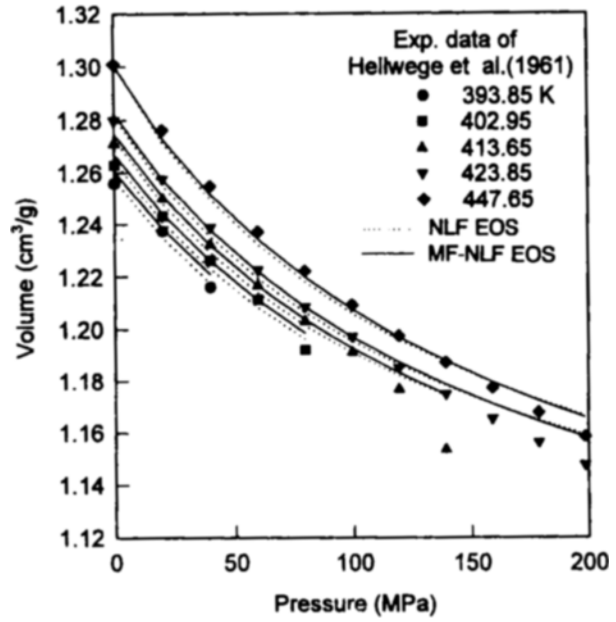

Fig. 2. Calculated and experimental specific volumes of low-density poly(ethylene, LDPE) as functions of temperature and pressure.

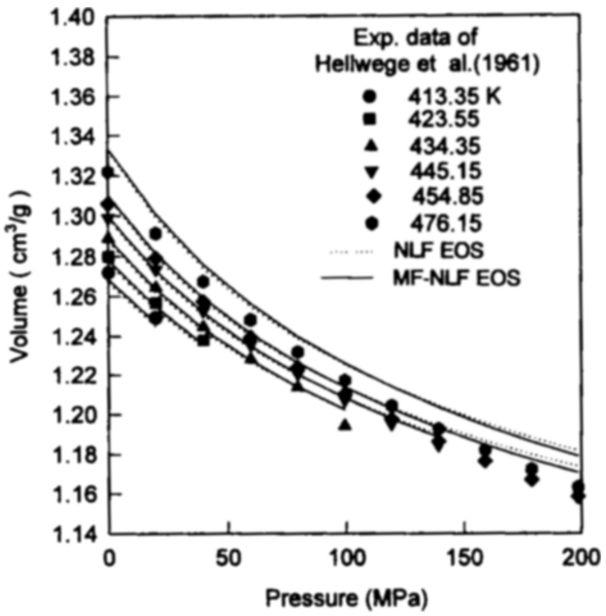

Fig. 1. Calculated and experimental specific volumes of high-density poly(ethylene, HDPE) as functions of temperature and pressure.

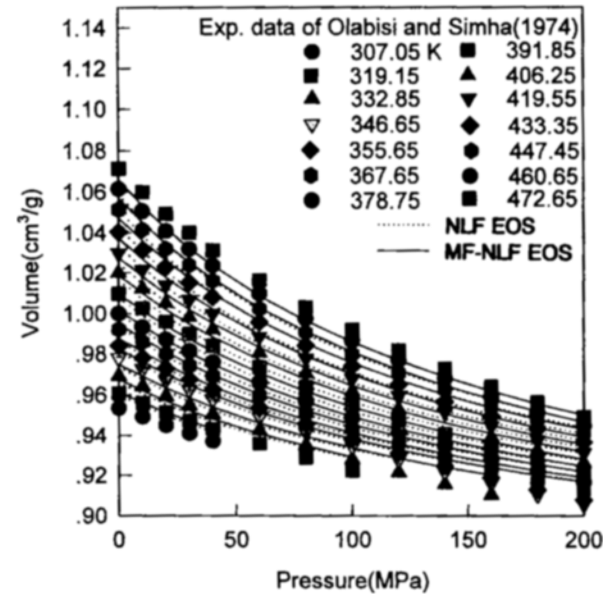

Fig. 3. Calculated and experimental specific volumes of poly (n-butyl methacrylate, PnBMA) as functions of temperature and pressure.

In Fig. 3, the experimental and calculated specific volumes

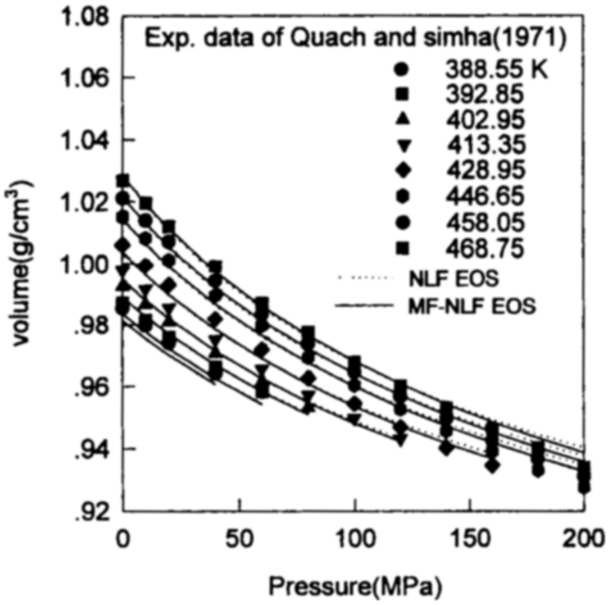

Fig. 4. Calculated and experimental specific volumes of poly (styrene, PS) as functions of temperature are pressure.

by NLF (AAD=0.577) and MF-NLF (AAD=0.419) of poly(n-butyl methacrylate, PnBMA) [Olabisi and Simha, 1975] are shown. Both models predict the volumetric properties of PnBMA quantitatively well enough for the purpose of engineering calculations.

As final demonstrations of the applicability of the NLF and the MF-NLF to the volumetric properties of polymers, the calculated results for poly(styrene, PS) [Quach and Simha, 1971] and poly(o-methylstyrene) [Quach and Simha, 1971] are shown in Figs. 4 and 5, respectively.

Since we have demonstrated elsewhere in detail [You et al., 1993, 1994a, b; Yoo et al., 1995a, b, c] the theoretical soundness of both EOSs and their advantages over the existing models in the same genre, such as the EOSs after Sanchez and Lacombe [1977], Panayiotou and Vera [1982], and Kumar et al. [1987], we omit here further comparisons of the practical applicability of the two models with other existing models.

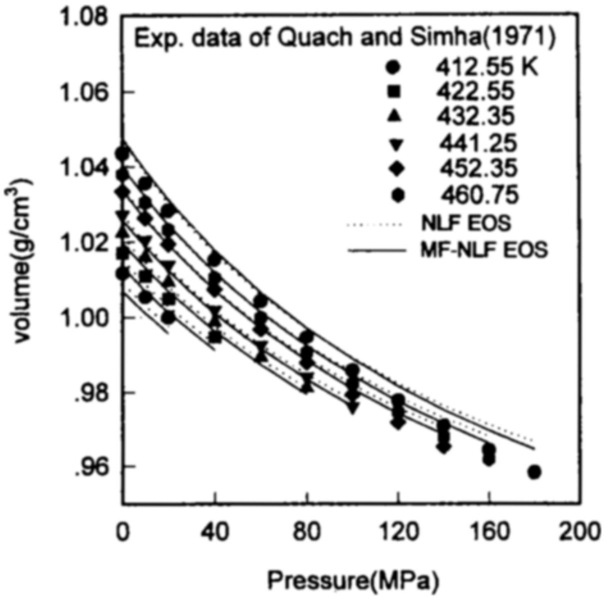

Fig. 5. Calculated and experimental specific volumes of poly (o-methylstyrene) as functions of temperature and pressure.

CONCLUSION

We have demonstrated the practical applicability of the NLF and the MF-NLF EOSs to the calculation of specific volumes of common pure polymers. The advantage of the NLF is that it is based on a sound statistical-mechanical basis of nonrandom lattice-hole theory after Guggenheim [Guggenheim, 1952]. However, the MF-NLF model is based on a semi-theoretical improvement of the lattice-hole by the introduction of a nonrandom two-fluid approximation with respect to the residual nonrandomness contribution. Thus, the expression of the MF-NLF is much simpler than that of the NLF.

We found that both models appear to be equally applicable to engineering-oriented volumetric properties calculations of various polymer systems. As for the preferential utilization of the NLF or the MF-NLF models, the present authors wish to leave that to the users.

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NOMENCLATURE

E_a : coefficient in Eq. (8) [–]
k : Boltzmann factor [JK^{-1}]
N_A : Avogadro's number [mol^{-1}]
P : pressure [MPa]
q : segment surface area parameter [–]
r : segment number [–]
T : temperature, T_0 = reference temperature, 298.15 [K]
V : system volume [cm^3]
V_a : coefficient in Eq. (9) [–]
V_H : unit lattice cell volume [cm^3]
z : coordination number [–]

Greek Letters

α_1 : thermal expansivity [K^{-1}]
β : Boltzmann factor, =1/kT [–]
β_1 : isothermal compressibility factor [bar^{-1}]
ε_{11} : molecular interaction energy between molecules 1 [–]
θ_0 : effective surface area fraction of holes [–]
θ_1 : effective surface area fraction of component 1 [–]
ρ : system density [$1/cm^3$]
τ_{01} : nonrandomness factor between hole, 0, and occupied molecule, 1 [–]

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