J. Phys. Chem. B **2009,** *113,* 11977–11987

An Accurate Equation of State for Fluids and Solids

G. A. Parsafar*

Department of Chemistry, Sharif University of Technology, Tehran, Iran

H. V. Spohr and G. N. Patey*

Department of Chemistry, University of British Columbia, Vancouver BC, Canada V6T 1Z1

Received: April 16, 2009; Revised Manuscript Received: June 26, 2009

A simple functional form for a general equation of state based on an effective near-neighbor pair interaction of an extended Lennard-Jones (12,6,3) type is given and tested against experimental data for a wide variety of fluids and solids. Computer simulation results for ionic liquids are used for further evaluation. For fluids, there appears to be no upper density limitation on the equation of state. The lower density limit for isotherms near the critical temperature is the critical density. The equation of state gives a good description of all types of fluids, nonpolar (including long-chain hydrocarbons), polar, hydrogen-bonded, and metallic, at temperatures ranging from the triple point to the highest temperature for which there is experimental data. For solids, the equation of state is very accurate for all types considered, including covalent, molecular, metallic, and ionic systems. The experimental *pvT* data available for solids does not reveal any pressure or temperature limitations. An analysis of the importance and possible underlying physical significance of the terms in the equation of state is given.

I. Introduction

In an extensive review published in 1969, Macdonald[1] suggested that the existence of a usefully simple equation of state (EoS) that applies consistently to all dense matter is extremely unlikely. This opinion was perhaps based on the fact that dense systems are complicated at the molecular level with diverse many-body interactions, and moreover, even the pair interactions are not well-known, except for the simplest systems. Nevertheless, at present, there exist several equations of state that are reasonably accurate for a variety of dense materials.[2−12]

Despite their complexity at the molecular level, dense systems exhibit a number of simple regularities,[13,14] some of which have been known experimentally for a long time. The existence of these regularities suggests that it might be possible to write a general effective potential that embodies the common features that appear in the equations of state of many different materials. On the basis of this reasoning, several effective, near-neighbor pair potentials have been introduced in the literature, and associated equations of state have been derived.[7,9−12] This work has provided simple analytical forms for equations of state that can accurately "fit" experimental data for a varied selection of materials and over significant ranges of state parameters.

For some dense fluids, it is known experimentally that isotherms plotted as $(Z - 1)v^2$ versus ρ^2, where Z is the compressibility factor, ρ is the density, and v the molar volume, tend to be linear. Parsafar et al.[10,15] employed an effective potential of the Lennard-Jones (LJ)(12,6) type (originally named the averaged effective pair potential) to obtain an equation of state that mimics this behavior. Ghatee and Bahadori[11] proposed using the softer Mie(6,3) potential to obtain an accurate equation of state for liquid cesium and other liquid metals. Parsafar and Mason[9] used the repulsive branch of a universal expression for the binding energy of solids given by Rose et al.[16] to obtain a simple cubic function for the potential energy in terms of density. Recently, Shokouhi et al.[12] have shown that the effective pair potentials that have been proposed for dense fluids are also appropriate for some solids.

The purpose of the present paper is to suggest a new, more general equation of state that works extremely well for a great variety of fluids and solids and over wide ranges of density. Indeed, we have not yet found a material for which it fails. The validity of the equation of state is tested using experimental *pvT* data for fluids and solids that have very different physical properties, ranging from neon to long-chain hydrocarbons to ionic and metallic solids. Computer simulation results for ionic liquids are also used to provide further tests and to investigate the relative importance of the internal and thermal pressure contributions to the thermodynamic equation of state. Expressions for the temperature dependence of the parameters (three in total) that occur in the equation of state are also given. Finally, the new equation of state is compared with some earlier suggestions.

II. The Equation of State

We define the intensive quantities $v = V/N$ and $u = U/N$, where V is the volume and U the configurational (potential) energy of a N particle system. Then, an exact thermodynamic equation of state can be written as

$$p = T\left(\frac{\partial p}{\partial T}\right)_v - \left(\frac{\partial u}{\partial v}\right)_T \tag{1}$$

where p is the pressure, T the temperature, and we have used the fact that the ideal contribution to the total internal energy is independent of density. The first and second terms of eq 1 are often named the thermal and internal pressures, respectively. Following Parsafar and Mason,[10] we rewrite eq 1 in the form

---

* To whom correspondence should be addressed. E-mail: parsafar@sharif.edu (G.A.P.); patey@chem.ubc.ca (G.N.P.).

10.1021/jp903519c CCC: $40.75

$$(Z - 1)v^2 = -\frac{1}{\rho^3 k_B T}\left(\frac{\partial u}{\partial v}\right)_T + a_2 \tag{2}$$

where

$$a_2 = \frac{1}{\rho^2}\left[\frac{1}{\rho k_B}\left(\frac{\partial p}{\partial T}\right)_v - 1\right] \tag{3}$$

is the contribution from the nonideal thermal pressure (following the notation of Parsafar and Mason[10]), $Z = pv/k_BT$ is the compressibility factor, $\rho = 1/v$ is the number density, and k_B is the Boltzmann constant.

Parsafar and Mason[10] suggested evaluating the first term on the right-hand side of eq 2 by introducing an effective near-neighbor pair potential. Following their approach, and also the more recent work of Ghatee and Bahadori,[11] aimed at finding an equation of state for liquid metals, we propose a more general effective near-neighbor pair potential, such that the total configurational energy of an N particle system is given by

$$U = \frac{N}{2}z\left(\frac{C_{12}(T)}{r^{12}} + \frac{C_6(T)}{r^6} + \frac{C_3(T)}{r^3}\right) \tag{4}$$

In eq 4, r is taken to be a mean near-neighbor distance, and following Parsafar and Mason,[10] we assume that $r \approx v^{1/3}$. The parameter z is the mean coordination number, which, for solids, will obviously be constant if no phase transition occurs in the density range of interest. For a fluid, if one defines the distance r as fixed, independent of density, then one would expect z to vary with ρ. However, in the present model, where it is assumed that $r \approx v^{1/3}$, z will also be independent of density for fluids.

Substituting $r = v^{1/3}$ into eq 4 and differentiating, we obtain

$$\left(\frac{\partial u}{\partial v}\right)_T = -\left(\frac{D_{12}(T)}{v^5} + \frac{D_6(T)}{v^3} + \frac{D_3(T)}{v^2}\right) \tag{5}$$

where the $D_i(T)$ are temperature-dependent parameters. In our model, eq 2 now becomes

$$(Z - 1)v^2 = F_6(T) + \frac{F_3(T)}{\rho} + F_{12}(T)\rho^2 + a_2 \tag{6}$$

where the parameters $F_i(T)$ are related to the corresponding r^{-i} terms in the effective potential.

It is useful at this point to consider earlier work[10,11] in more detail. In their original paper, Parsafar and Mason[10] assumed an effective potential of the LJ(12,6) form with temperature-independent parameters (i.e., the first two terms of eq 4 with temperature-independent C_i). They further assumed that the term related to the thermal pressure coefficient (the last term) in eq 6 is a constant, independent of density over the density range of interest. This latter assumption will be further discussed below. With these assumptions, Parsafar and Mason[10] obtained the result

$$(Z - 1)v^2 = a + b\rho^2 \tag{7}$$

where $a = a_2 + a_1/T$, $b = b_1/T$, a_1 and b_1 are related to the attractive and repulsive terms of the effective potential, respectively, and a_2 is the contribution coming from the nonideal thermal pressure, as defined above.

Equation 7, which is known as the linear isotherm regularity,[10] will be referred to as EoS I in this paper. This equation of state has been used to explain some experimentally well-known regularities and also to predict some that were previously unknown.[17,18] Equation 7 is valid for densities higher than the Boyle density, $\rho_B \simeq 1.8\rho_C$, and temperatures less than twice the Boyle temperature, $T_B \simeq 2.5 - 2.7T_C$, where ρ_C and T_C are the critical density and temperature, respectively. It was recently shown[12] that EoS I works well for some nonionic and nonmetallic solids, as well as for dense fluids. Equation 7 does show some deviations from experiment for extremely nonspherical molecules. Parsafar and Klantar[19,20] have shown that the $(Z - 1)v^2$ versus ρ^2 isotherms for long-chain organic compounds show significant deviations from linearity. Moreover, we show below that, somewhat unexpectedly, EoS I cannot fit the data for the simple fluid neon if a wide density range is considered (see section IV.A). Also, the application of EoS I to alkali metals, more specifically, liquid cesium, suffers within the density range where the metal–nonmetal transition occurs.[11,21]

To find an equation of state for liquid metals, in particular, liquid cesium, Ghatee and Bahadori[11] proposed that an effective potential of the Mie(6,3) form be used, again with temperature-independent coefficients. Their arguments for this form are based on the effective potential obtained by inverting the structure factor of liquid cesium. In particular, Ghatee and Bahadori[11] suggested that the Mie(6,3) potential would "soften" the core repulsion and that the r^{-3} term would help account for the longer-ranged, slowly decaying interaction found for liquid cesium.[22] Using arguments analogous to those of Parsafar and Mason,[10] including the assumption that the last term in eq 6 is independent of density, Ghatee and Bahadori[11] obtained the equation of state

$$(Z - 1)v^2 = c + \frac{d}{\rho} \tag{8}$$

where $c = a_2 + c_1/T$ and $d = d_1/T$, with d_1 and c_1 related to the attractive and repulsive parts of the effective potential, respectively. Here, we shall refer to eq 8 as EoS II. Ghatee and Bahadori[11] showed that EoS II gives a good description of the equation of state for cesium over its entire liquid range. Recently, it has been shown that EoS II is valid for some metallic and ionic solids as well.[12]

Despite the success of EoS I for many atomic and molecular liquids and solids and of EoS II for some metals and ionic systems, there remain many materials for which neither equation of state works well, especially if wide density ranges are considered (see section IV). This has led us to seek a more general result.

The effective pair potential that we assumed above (eq 4) is of an extended Lennard-Jones (ELJ)(12,6,3) form with temperature-dependent coefficients. A motivation for this form is that it yields an equation of state with both the ρ^2 dependence of EoS I and the $1/\rho$ dependence of EoS II. Physically, terms proportional to r^{-6} and r^{-12} can be justified in an effective potential because a dispersion interaction, together with a term representing the repulsive cores, is expected to be present for molecules of all types. The r^{-3} term, which gives the $1/\rho$ contribution in eq 6, is harder to rationalize because, apart from molecules with permanent dipoles, we would not expect a term proportional to r^{-3} in the true pair potential. However, here, we are considering a model where the total configurational

TABLE 1: Parameters in the Fits of Equations 9 and 11 to the Ionic Liquid Results[a]

T, K	k_6/k_BT	k_3/k_BT	k_{12}/k_BT	R^2 (eq 11)	e	f	g	R^2 (eq 9)
1200	24.550	−28.238	−6.1938	0.99999	6.0130	−9.6755	3.3172	0.99998
1700	14.294	−18.019	−2.8984	0.99997	5.8244	−7.1891	2.2238	0.99998
2000	11.968	−15.008	−2.4001	0.99996	5.7381	−6.2745	1.7719	0.99998

[a] R^2 is the coefficient of determination for the fits indicated. The reduced density (ρ^*) ranges used in the fits are 0.7005−0.8993 at 1200 K and 0.7005−1.0244 at 1700 and 2000 K.

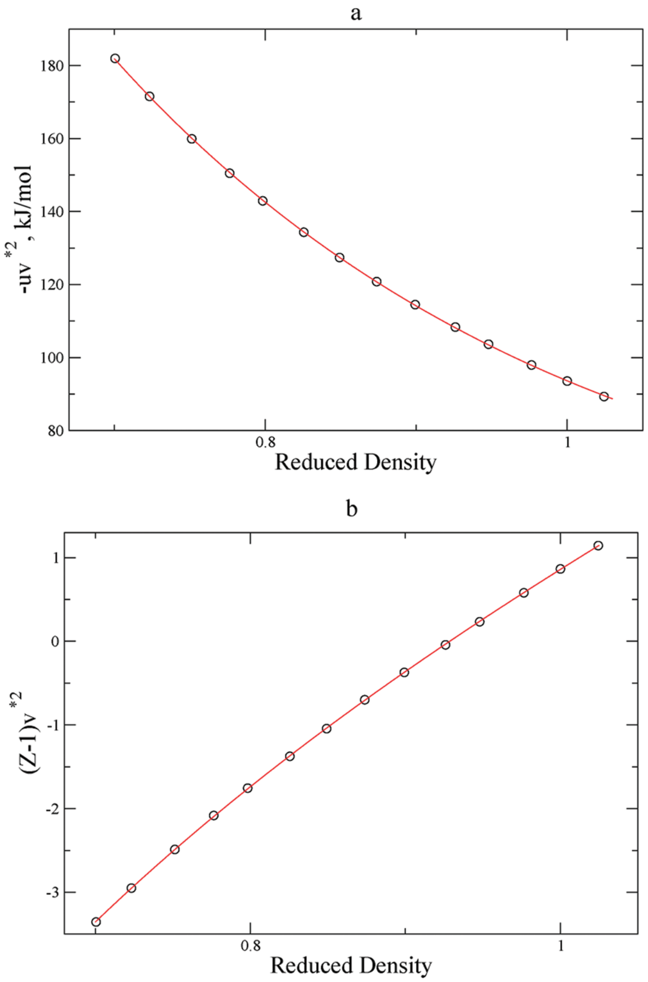

Figure 1. Simulation results for the model ionic liquid at 1700 K. The solid curves represent fits to (a) eq 11 and (b) eq 9. Note that $v^* = 1/\rho^*$.

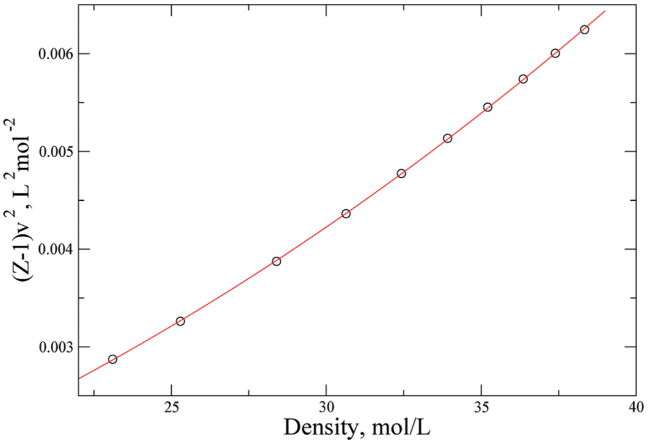

Figure 2. Testing EoS III at high density. The points are experimental values for CO,[25] and the solid curve is the fit to eq 9.

TABLE 3: Examing Equation 9 for Any Low-Density Limitation[a]

substance	T, K	$\Delta\rho$, mol/L	R^2
CH_4	150	22.3796−30.2510	1.0000
	190	7.21135−33.2518	0.99635
	190	15.0030−33.2518	0.99972
	190	17.6148−33.2518	0.99997
	308.15	23.3716−35.3615	0.99996
	473.15	21.1042−33.0584	0.99994
	500	10.0625−32.144	0.99996
N_2	100	24.584−34.576	0.99991
	400	11.376−36.184	0.99996
	600	5.2407−33.237	0.99992
	600	9.1343−33.237	0.99972
	600	11.187−33.237	0.99969
	800	13.641−30.967	0.99952
	1200	10.335−26.194	1.0000

[a] $\Delta\rho$ denotes the density range used in the fit, and R^2 is the coefficient of determination associated with the fit.

energy is represented by effective near-neighbor interactions. Thus, one can simply view the r^{-3} term as a "stand in" for all contributions to the energy that cannot be represented by the LJ(12,6) interaction. In practice, we find that the $1/\rho$ term appears essential in a general equation of state, and within the assumptions of Parsafar and Mason,[10] this term can come only through an r^{-3} contribution in the effective potential. It is also worth noting that for systems of uncharged particles, the leading term in the exact low-density expansion of $(Z - 1)v^2$ behaves as $1/\rho$. Thus, for such systems, a term proportional to $1/\rho$ is necessary to ensure that the equation of state obeys the correct low-density limit. A further discussion of the importance of the $1/\rho$ term in EoS III and why it may appear very significant for some materials but not for others is given below (section IV).

Further consideration of the contribution of the a_2 term in eq 6 is also necessary. In their original work, Parsafar and Mason[10] assumed that a_2 is nearly independent of density. They based their assumption mainly on experimental results for argon, and it may well be a good approximation for many materials. However, using computer simulations, we show explicitly that it does not hold at all for model ionic liquids. As discussed below (section III), for ionic liquids, the density dependence of

TABLE 2: Contributions of the Internal and Nonideal Thermal Pressures to the Coefficients of EoS III for Model Ionic Liquids

T, K	$2k_6/k_BT$	$(e - 2k_6/k_BT)$	k_3/k_BT	$(f - k_3/k_BT)$	$4k_{12}/k_BT$	$(g - 4k_{12}/k_BT)$
1200	49.10	−43.09	−28.24	18.56	−24.78	28.09
1700	28.59	−22.76	−18.02	10.83	−11.59	13.82
2000	23.94	−18.20	−15.01	8.734	−9.600	11.37

a_2 is comparable to that of the internal pressure contribution and follows the same functional form.

Thus, we express eq 6 as

$$(Z - 1)v^2 = e + \frac{f}{\rho} + g\rho^2 \tag{9}$$

where e, f, and g are nontrivial functions of temperature, and in general, one must expect all three functions to contain contributions from both the internal and thermal pressures. We call eq 9 EoS III, and it is the central result of this paper. We show below that it gives an excellent representation of isotherms for widely differing materials and over wide ranges of density. We note that the accuracy of EoS III also extends to ionic liquids, even though for Coulombic systems, we would expect (assuming complete dissociation of the ions) the low-density limit to behave as $\rho^{-3/2}$ rather than ρ^{-1}. A brief discussion of a model ionic liquid to illustrate the density dependence of a_2 is given below. A complete analysis of the application of EoS III to ionic liquids including further model calculations and experimental results will be given in a forthcoming paper.[23]

III. Computer Simulation Results for a Model Ionic Liquid: The Density Dependence of a_2

A detailed description of molecular dynamics (MD) results for model ionic liquids of different types will be given elsewhere.[23] Here, it is useful to briefly discuss one relatively simple model in order to demonstrate that a_2 can be strongly density-dependent for some systems. We consider a model ionic liquid consisting of equal size LJ spheres embedded at the center with single elementary charges such that the interaction of ions i and j is given by

$$u(ij) = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \tag{10}$$

where $\epsilon = 3.614$ kJ/mol and $\sigma = 0.5$ nm are the LJ energy and length parameters taken to be the same for all pair interactions, r_{ij} is the distance between the centers of mass of ions i and j, and ϵ_0 is the permittivity of free space. Molecular dynamics simulations were carried out at three temperatures, 1200, 1700, and 2000 K, for a range of reduced densities, $\rho^* = \rho\sigma^3$, where $\rho = (N_+ + N_-)/V$ is the number density. Note that the densities used (Table 1) are typical liquid values. A significant advantage of computer simulations is that one obtains both the configurational energy and the pressure. This allows us to separate the contributions of the internal and thermal pressure terms to the equation of state.

The expressions for the configurational energy and equation of state given above were obtained explicitly for one-component systems, but as shown by Parsafar and Mason,[24] analogous expressions can be found for multicomponent (constituent) systems. For the present discussion, it is convenient to rearrange eq 4 into the form

$$uv^2 = k_6 + \frac{k_3}{\rho} + k_{12}\rho^2 \tag{11}$$

where the k_i are temperature-dependent coefficients. Then, combining eqs 2, 9, and 11 immediately gives the nonideal thermal contribution in the form

TABLE 4: Parameters of Equation 9 and Coefficients of Determination for Different Isotherms of Nitrogen Over the Pressure Range Δp

T, K	e, (L/mol)^2	f, (L/mol)	g, (L/mol)^4	Δp, MPa	R^2
100	-0.0158518	0.144462	1.39049×10^{-5}	0.8−200	0.99991
200	-9.62551×10^{-4}	-6.25806×10^{-3}	5.43791×10^{-6}	20−900	0.99957
308.15	1.31533×10^{-3}	-6.63055×10^{-3}	3.22340×10^{-6}	150−1000	0.99995
400	1.28451×10^{-3}	9.82150×10^{-3}	2.59806×10^{-6}	50−900	0.99996
600	1.44183×10^{-3}	0.0201100	1.78244×10^{-6}	80−900	0.99969
800	1.42354×10^{-3}	0.0250311	1.34165×10^{-6}	150−900	0.99952
1000	1.34963×10^{-3}	0.0280700	1.05946×10^{-6}	150−900	0.99997
1200	1.28708×10^{-3}	0.0297710	8.45318×10^{-7}	150−800	1.0000

TABLE 5: As in Table 2 but for Isotherm(s) of Different Fluids

fluid	T, K	$10^3 \times e$, (L/mol)^2	$10^2 \times f$, (L/mol)	$10^6 \times g$, (L/mol)^4	Δp, MPa	R^2
Ar[a]	120	−7.91713	5.77526	5.66745	1.5−150	0.99999
Ar[b]	308.15	0.00258067	0.119478	1.93337	150−1000	0.99999
Ne[c]	298	0.287237	1.10615	0.058911	60−1000	0.99949
N_2[d]	308.15	1.31533	−0.663055	3.22340	150−1000	0.99995
CO[e]	308.15	1.47330	−1.01608	3.43530	150−1000	0.99995
CH_4[f]	150	−15.6599	9.87947	18.6804	1.5−200	1.0000
	308.15	−0.467732	−1.66984	7.18707	150−1000	0.99996
	500	1.12743	0.226194	4.28628	50−1000	0.99996
C_3H_8[g]	308.15	−57.5237	20.0147	238.882	100−1000	0.99996
n-C_9H_{20}[h]	303.15	−3913.32	1068.35	63650.7	20−620	1.0000
n-$C_{19}H_{40}$[i]	343.15	−34315.4	4946.29	2117410	0.1−150	1.0000
CH_3OH[j]	300	−25.4517	18.2106	27.2493	0.15−70	1.0000
H_2O[k]	298.15	0.928970	−15.1403	0.484137	20−800	1.0000
Hg[k]	303.15	−25.8876	43.4644	4.23011	100−800	0.99999

[a] Reference 30. [b] Reference 31. [c] Reference 37. [d] Reference 29. [e] Reference 25. [f] References 26 and 27. [g] Reference 32. [h] Reference 33. [i] Reference 34. [j] Reference 35. [k] Reference 36.

$$a_2 = e - \frac{2k_6}{k_B T} + \left(f - \frac{k_3}{k_B T}\right)\frac{1}{\rho} + \left(g - \frac{4k_{12}}{k_B T}\right)\rho^2 \tag{12}$$

Given that eq 2 is exact, if the equation of state is well fit by eq 9 and if the configurational energies are well fit by eq 11, then eq 12 must give an accurate representation of the nonideal thermal pressure contribution.

The fitting parameters and R^2 values for both the energy (eq 11) and EoS III (eq 9) are given in Table 1 for three temperatures. Note that for these fits, the density was expressed in reduced units ($\rho^* = \rho\sigma^3$), such that the fitting parameters given in Table 1 are in dimensionless form. The fits obtained at 1700 K are shown in Figure 1, and similarly excellent fits were obtained at 1200 and 2000 K. We note that fits to EoS I and EoS II (not shown) do not give a good representation of the results; plots versus ρ^{*2} and $1/\rho^*$ show deviation from the linearity expected for EoS I and EoS II, respectively.

Considering the fits to eq 11, it is interesting to note (Table 1) that k_6 and k_3 are of similar magnitude but opposite sign. The k_6 term makes a positive contribution to the average configurational energy, and the k_3 and k_{12} terms make negative contributions, with k_{12} about an order of magnitude smaller than k_3. Thus, for our model ionic liquid, the main contributions to k_3 and k_{12} must come through the attractive LJ and Coulombic interactions, whereas k_6 is dominated by repulsions. We note that this pattern holds for the energies of other model ionic liquids not discussed in this paper. This serves to illustrate that, at least for ionic liquids, the terms in the effective near-neighbor potential may not have the same physical significance as terms with the same r dependence in the true pair interaction.

From the fitting parameters given in Table 1, we can easily obtain the coefficients of the internal and nonideal thermal pressure contributions to the equation of state. These are given in Table 2 for all three temperatures. Note that terms depending only on the k_i are the internal pressure coefficients and that the coefficients of the nonideal thermal pressure contribution are given in eq 12. From Table 2, we see that the coefficients associated with both contributions are of similar magnitude but opposite sign. It is clear that both terms in eq 2 contribute significantly to all three coefficients in EoS III.

IV. Comparison with Experimental Data

A. Fluids. We first examine eq 9 to check for temperature and/or density limitations. In order to test for limitations at high density, we use the CO data given by Robertson and Babb, Jr.[25] The 308.15 K isotherm is shown in Figure 2, and we note that eq 9 fits the data very well over the entire density range, 23−38 mol/L, with a coefficient of determination of $R^2 = 0.99995$. Similar results are found for other fluids, including CH_4, Ar, and N_2. Therefore, on the basis of the reported experimental data, there does not appear to be an upper density limit on the validity of eq 9, as long as the material remains fluid. A similar conclusion was reached[10] for EoS I.

To examine the lower density limit, we use experimental data for CH_4, both the revised data given by Robertson,[26] and the summary of Setzmann and Wagner.[27] We also use the N_2 data as summarized by Jacobsen et al.[28] The R^2 values obtained for different isotherms, together with the density ranges used in each fit to eq 9, are given in Table 3. We consider the fit to be "very good" if $1 - R^2 < 0.001$. We see from Table 3 that the fits are very good for all isotherms, at least for densities larger than the critial density (the critical density and temperature[27,28] for CH_4 are 10.150 mol/L and 190.564 K, and those for N_2 are 11.177 mol/L and 126.1 K). For supercritical isotherms, the fits are good at much lower densities, for example, see the different density ranges fit for N_2 at 600 K. Thus, generally speaking, we may consider the critical density as the lower density limit of eq 9 for isotherms near the critical temperature.

To look for possible temperature limitations of EoS III, we use the nitrogen data given in ref 28 (for a wide range of

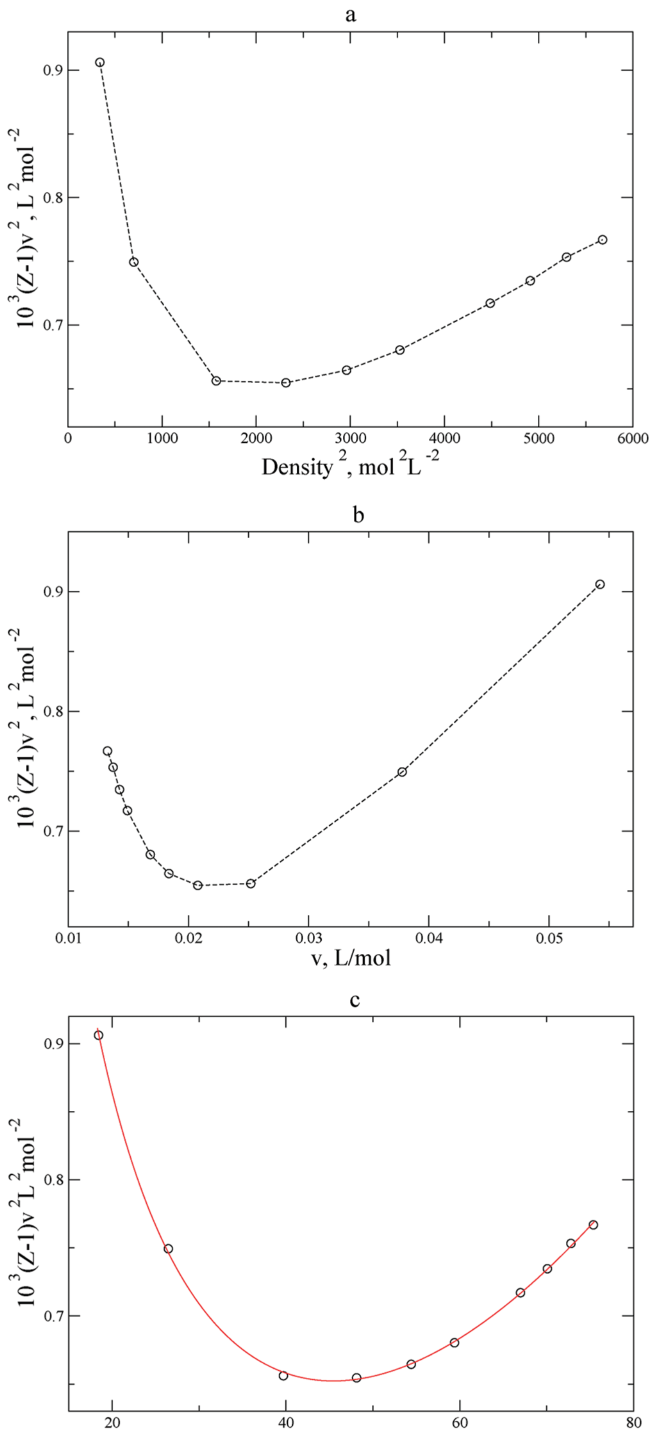

Figure 3. The 298 K isotherm of fluid neon. The points are experimental results,[37] and in (a) and (b), the dashed lines are simply to guide the eye. The solid line in (c) is the fit to EoS III (eq 9). Plots (a) and (b) show that both EoS I and EoS II, respectively, deviate significantly from linearity, whereas plot (c) shows that EoS III gives an excellent fit to the data.

TABLE 6: The Contributions of the f/ρ and $g\rho^2$ Terms in EoS III for n-$C_{19}H_{40}$ (343.15 K), H_2O (298.15 K), and Au (300 K) at Selected Densities

substance	ρ, (mol/L)	f/ρ, $(L/mol)^2$	$g\rho^2$, $(L/mol)^2$
n-$C_{19}H_{40}$	2.786	17.75	16.43
	2.864	17.27	17.37
	2.945	16.80	18.36
	3.010	16.43	19.18
	3.065	16.14	19.89
H_2O	55.8300	-2.712×10^{-3}	1.509×10^{-3}
	59.5131	-2.544×10^{-3}	1.715×10^{-3}
	62.5623	-2.420×10^{-3}	1.895×10^{-3}
	65.0000	-2.330×10^{-3}	2.046×10^{-3}
	67.0500	-2.258×10^{-3}	2.177×10^{-3}
Au(s)	99.89	-65.45×10^{-3}	3.199×10^{-3}
	108.8	-60.11×10^{-3}	3.793×10^{-3}
	119.4	-54.76×10^{-3}	4.569×10^{-3}
	132.3	-49.42×10^{-3}	5.610×10^{-3}
	148.3	-44.08×10^{-3}	7.053×10^{-3}

temperatures) and ref 29. The fitting results are summarized in Table 4, and it is evident that eq 9 gives very good fits for all isotherms considered. Hence, at least as far as can be checked with available experimental data, EoS III does not have any temperature limitation.

We have used experimental pvT data for widely varying fluids[25−27,29−37] to investigate the generality of EoS III. The results for different selected fluids are given in Table 5, and these serve to demonstrate the generality of EoS III. In comparison, we note that EoS II does not fit the experimental data for atomic and molecular fluids at all, and EoS I shows some deviation for water, long-chain hydrocarbons, and metallic liquids.

In fact, if a wide enough density range is considered, one does not have to consider more complex fluids to find an example where both EoS I and EoS II cannot fit the data. Results for supercritical neon[37] at 298 K are plotted over a wide density range in Figure 3a−c. The function $(Z - 1)v^2$ versus density passes through a minimum, and it is obvious that neither EoS I nor EoS II can describe this behavior. On the other hand, EoS III again gives an excellent fit over the entire density range. Some insight into the possible reason for the neon behavior, and why it differs from some other simple fluids such as argon, can be gleaned by expanding the van der Waals expression for $(Z - 1)v^2$ to obtain

$$(Z - 1)v^2 = b^2 + \left(b - \frac{a}{RT}\right)\frac{1}{\rho} + b^3\rho + b^4\rho^2 + ... \tag{13}$$

where b and a are the usual van der Waals parameters associated with replusive and attractive interactions, respectively. We note that a term linear in ρ does not occur in EoS III and appears unncessary to fit experimental data for dense matter. The term proportional to $1/\rho$ is interesting in that at the van der Waals level, it is the only term that depends on both b and a, and clearly if the terms b and a/RT largely cancel, the $1/\rho$ contribution will be unimportant. However, if for particular materials the cancellation is insufficient, the $1/\rho$ term will be significant and perhaps even dominate, giving the behavior predicted by EoS II. Possibly, for argon and other systems where EoS I works well, there is a good deal of cancellation between repulsive and attractive forces in dense fluids, as was noted by Parsafar and Mason in their original paper.[10] For neon, the dispersion interaction is weaker than that for argon and is possibly too small to cancel the repulsive contribution; thus, the $1/\rho$ term is important. The van der Waals expression suggests that the $1/\rho$ term will be significant whenever the attractive and repulsive contributions do not largely cancel. Of course, we know that the van der Waals equation does not apply to dense fluids and solids, but it does offer some explanation as to why a $1/\rho$ term is apparently necessary in the equation of state for some materials but is unimportant for others.

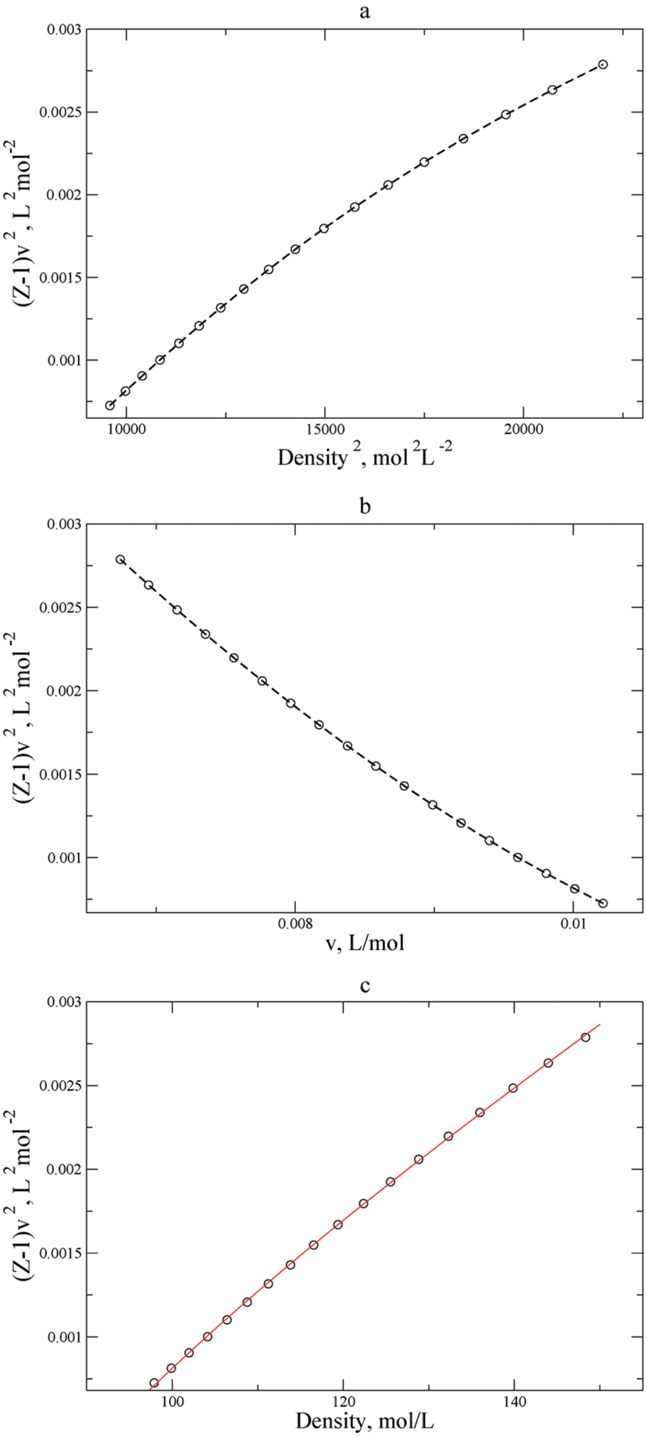

Figure 4. As in Figure 3, except that the data shown are for the 3000 K isotherm of solid gold.[38]

It is interesting to examine the contributions of f/ρ and $g\rho^2$ to EoS III. Note that if $g\rho^2$ dominates f/ρ over the entire density range, then EoS I will be sufficient; if the reverse is true, EoS II will apply, but if both terms are significant EoS III is necessary

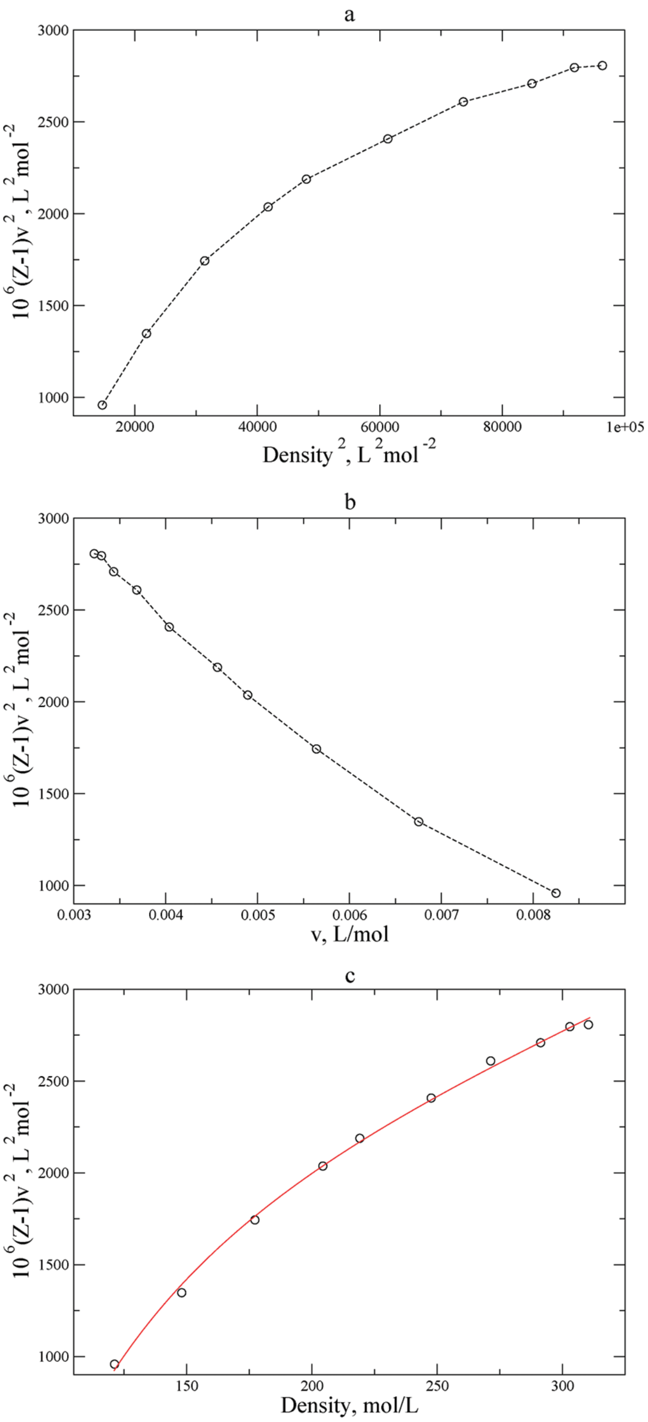

Figure 5. As in Figure 3, except that the data shown are for the 298 K isotherm of solid neon.[39]

to accurately describe the equation of state. As examples, results for two fluids (water and n-$C_{19}H_{40}$) and one solid (gold) are given in Table 6. For each substance, values are given for a range of densities on a particular isotherm. We see that for n-$C_{19}H_{40}$ and water, both terms are of comparable magnitude, which means that neither EoS I nor EoS II can provide an accurate description of the equation of state for these substances. However, for gold, the magnitude of $g\rho^2$ tends to be much smaller than that of f/ρ, particularly at low densities. Therefore, we would expect EoS II to be accurate for gold, at least if the densities are sufficiently low.

B. Solids. EoS I and EoS II were initially derived for atomic and molecular[10] and metallic[11] fluids, respectively, but were later applied to ionic, metallic, and other types of solids[12] as well. Even though EoS I and EoS II are relatively simple two-parameter equations of state, their accuracy is comparable with that of other well-known equations of state for solids.[12] Therefore, we compare the accuracy of EoS III with that of EoS I and EoS II. For comparison purposes, we use three different types of solid for which very high pressure data is available, specifically, gold, neon, and diamond.

Results for the 3000 K isotherm of gold are shown in Figure 4a−c using the experimental data of Heinz and Jeanloz.[38] Note that linear behavior is expected in Figure 4a if EoS I is obeyed and in Figure 4b if EoS II applies. We see that Figure 4a exhibits a significant convex deviation from linearity, which is to be expected because EoS I was not proposed for metals but for simpler liquids and solids.[10,12] The coefficient of determination for the linear fit is low ($R^2 = 0.99139$). Figure 4b exhibits a concave deviation from the expected linear behavior, with $R^2 = 0.99394$. Figure 4c shows that the experimental data are well fit by EoS III, with $R^2 = 0.99984$.

The data of Dewaele et al.[39] are used to make a similar comparison for solid neon, and the isotherm at 298 K is plotted in Figure 5a−c. A large convex deviation from EoS I is seen in Figure 5a, and an attempted fit gives $R^2 = 0.94312$. Figure 4b shows a smaller concave deviation from EoS II ($R^2 = 0.99477$). Again, EoS III gives a good fit (Figure 5c) with $R^2 = 0.99824$. Similar results are obtained for diamond, as shown by the 298 K isotherm[39] plotted in Figure 6a−c. In the diamond case, the deviations from EoS I and EoS II are smaller than those observed for neon (Figure 5a and b), which may be due to the smaller pressure range covered by the available experimental data.

We have examined the validity of EoS III for other solids as well, and the fits obtained are very good in most cases. Information about the fits for different solids and isotherms[38−47] is given in Table 7. We note that for the two oxides included (CaO and MnO), "noise" is apparent in the experimental data, and this results in R^2 values which deviate further from unity than is the case for the other solids considered. For solids, we conclude that the available experimental data do not reveal any pressure or temperature limitations for EoS III.

Expressions for the bulk modulus B and its pressure derivative B' can be easily obtained from EoS III. One obtains

$$B = \rho_0 RT\,[\rho_r + 2(f\rho_0)\rho_r^2 + 3(e\rho_0^2)\rho_r^3 + 5(g\rho_0^4)\rho_r^5] \tag{14}$$

and

$$B' = \frac{\rho_0 RT}{B}[\rho_r + 4(f\rho_0)\rho_r^2 + 9(e\rho_0^2)\rho_r^3 + 25(g\rho_0^4)\rho_r^5] \tag{15}$$

where $\rho_0 = 1/v_0$ is the molar density at $p = 0$ and $\rho_r = \rho/\rho_0$. The values of B and B' at zero pressure (B_0 and B_0') can be obtained simply by setting $\rho_r = 1$ in eqs 14 and 15. The values obtained for a range of solids at particular temperatures are given in Table 8 and compared with some literature values obtained using other equations of state.[39,46−51] We note that the agreement is reasonable, given that estimates of B_0 and B_0' tend to vary considerably depending on how they are obtained.

V. Temperature Dependence of the Parameters of EoS III

A knowledge of the temperature dependence of the three parameters in EoS III would greatly increase its predictive power with minimal input data. This is especially important for geophysical applications, where knowledge of high-pressure and high-temperature behavior is often necessary but direct measurement is difficult.

Since the temperature dependence of the $C_i(T)$ coefficients in eq 4 is not known, exact expressions for the temperature dependence of the parameters in EoS III cannot be found. Nevertheless, we can obtain empirical expressions following an approach first used for solids[9] and then extended to fluids.[8] The exact thermodynamic equation of state (eq 1) can be written as[9]

$$T^2\left(\frac{\partial(p/T)}{\partial T}\right)_\rho = -\rho^2\left(\frac{\partial u}{\partial \rho}\right)_T \tag{16}$$

Parsafar et al.[8] have shown that the assumption that $u(T)$ is linear in T, which is a good approximation for solids above the Debye temperature, does not hold for fluids. However, at least for simple fluids such as argon, the temperature dependence can be well described with a quadratic form. Therefore, we adopt the form

$$u(\rho, T) = u_0(\rho) + u_1(\rho)T + u_2(\rho)T^2 \tag{17}$$

where the density-dependent coefficients, $u_i(\rho)$, depend on the physical properties of the system being considered. Substituting eq 17 into eq 16 and integrating yields

$$\frac{p}{T} = \rho^2 u_0'(\rho)\frac{1}{T} - \rho^2 u_1'(\rho)\ln T - \rho^2 u_2'(\rho)T + \zeta(\rho) \tag{18}$$

where the $u_i'(\rho)$ are density derivatives of the $u_i(\rho)$ and $\zeta(\rho)$ is an unknown function of density.

Equation 9 can be rearranged into the form

$$\frac{p}{T} = k_B(\rho + f\rho^2 + e\rho^3 + g\rho^5) \tag{19}$$

Then, requiring that the temperature dependence of eq 19 be the same as that of eq 18, we obtain

$$f = f_0 + f_1 T + \frac{f_{-1}}{T} + f_2 \ln T \tag{20a}$$

$$e = e_0 + e_1 T + \frac{e_{-1}}{T} + e_2 \ln T \tag{20b}$$

$$g = g_0 + g_1 T + \frac{g_{-1}}{T} + g_2 \ln T \tag{20c}$$

where the f_i, e_i, and g_i will be different for different materials.

As a test of the above analysis, we have attempted to fit the results for nitrogen given in Table 4 using eqs 20a–20c, and the fits are shown in Figure 7a–c. We see that the fits for parameters e (Figure 7a) and f (Figure 7b) are reasonable and that the fit for parameter g (Figure 7c) is excellent.

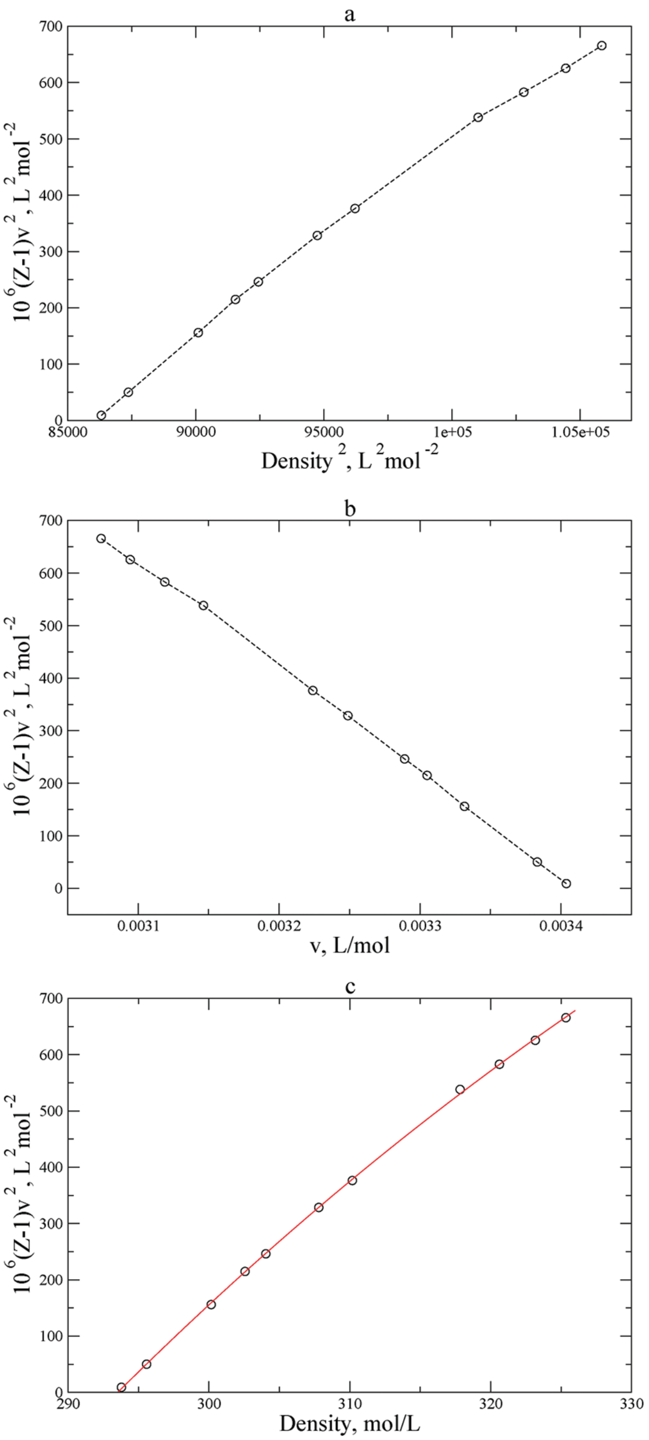

Figure 6. As in Figure 3, except that the data shown are for the 298 K isotherm of diamond.[39]

VI. Relative Importance of the Different Terms in EoS III for Different Materials

It is interesting to examine the relative magnitude of some coefficients in EoS III and compare them with corresponding coefficients in EoS I and EoS II. This gives some insight into the possible significance of the terms in the effective potential. The ratio $|g/f|$ is compared for different substances, all at a temperature near 300 K, in Table 9. Note that in Table 9, cesium chloride and all substances listed below it are solids, while all substances listed above CsCl are fluids. Also, keep in mind that the coefficients g and f are related to the ρ^2 and $1/\rho$ terms, respectively, in EoS III and that these terms are in turn related to the r^{-12} and r^{-3} parts of the effective potential.

TABLE 7: The Parameters of Equation 9 for Isotherms of Different Solids (quantities are tabulated as those in Table 4)

solid	T, K	Δp, GPa	$10^2 \times e$, (L/mol)^2	f, (L/mol)	$10^7 \times g$, (L/mol)^4	R^2
Ar[a]	65	0−1.863	−2.30982	−0.005696	128.377	0.99992
	77	0−1.863	−2.54504	0.280593	106.025	0.99970
H_2[a]	4	0−1.961	1.56376	−0.943934	2.27343	0.99658
D_2[a]	4	0−1.961	7.41524	−4.04448	13.8816	0.99856
Au[b]	300	3.56−216.10	6.35539	−6.53791	3.20568	0.99999
	3000	19.42−230.56	0.330025	−0.326071	0.772481	0.99984
Bi[c]	900	0−0.2	−0.0349846	−0.430555	43.6919	1.0000
NaCl[d]	300	1.385−20.907	20.5938	−7.54191	−25.9631	0.99999
CsCl[e]	293.15	2.50−45	60.7346	−15.2178	262.813	0.99965
$CaCO_3$[f]	300	0.001−300	89.9510	−25.4580	161.862	0.99973
H_2O[g]	250	0−0.200	2.66061	−1.47302	7.11374	1.0000
Ne[h]	298	4.53−208.8	0.316178	−0.281778	0.0609340	0.99824
C(diamond)[h]	298	1.3−57.6	1.15699	−2.97817	0.165238	0.99982
CaO(B_1)[i]	298	0−64.1	28.0180	−15.4144	−60.4568	0.99108
MnO[j]	300	0−60.5	13.8416	−10.6756	4.92582	0.98831

[a] Reference 40. [b] Reference 38. [c] Reference 41. [d] Reference 42. [e] Reference 43. [f] Reference 44. [g] Reference 45. [h] Reference 39. [i] Reference 46. [j] Reference 47.

TABLE 8: Bulk Moduli (B_0) and Their Pressure Derivatives (B_0') at $p = 0$ Obtained Using EoS III[a]

solid	T, K	B_0, kbar	B_0'
Ar	77	12.38(14.1)[b]	8.956
H_2	4	1.251(1.74)[c]	5.099(5.4)[c]
D_2	4	3.678(3.37)[c]	5.341(5.4)[c]
C(diamond)	298	4546(4445)[d]	3.841(4.18)[d]
Au	300	1698(1666.5)[e]	5.261(5.4823)[e]
CsCl	293	199.1(168)[e]	5.328(5.85)[e]
NaCl	300	243.7(235)[e]	4.765(5.35)[e]
CaO	298	1140(1147)[f]	4.390(4.10)[f]
MnO	300	1589(1620 ± 170)[g]	5.106(4.8 ± 1.1)[g]

[a] Results are included for selected solids and temperatures. Some values previously reported are given in parentheses. [b] Reference 48. [c] References 49 and 50. [d] Reference 39. [e] Reference 51 (note that for CsCl, the literature values are for 300 K). [f] Reference 46. [g] Reference 47.

Considering first the fluids, we note that $|g/f|$ tends to be largest for nonpolar molecules, and its magnitude has a rough correlation, with the particle "size" being largest for the long-chain hydrocarbons. This indicates that the r^{-12} term in the effective potential is relatively important for nonpolar species (especially large molecules), as one might have expected. For the polar species, methanol and water, the ratio is smaller and seems to decrease with polarity, with water having the lowest value of all liquids considered. The value for mercury is comparable to that of water. Thus, one is tempted to conclude that the r^{-3} term in the effective potential takes account of longer-ranged effects coming through the dipolar interactions in water and methanol and through other long-range correlations in liquid metals.[11] However, the low value for fluid neon (falling between mercury and water) appears to be a counterexample to this explanation. Perhaps the importance of the r^{-3} term is simply due to the fact that it introduces a $1/\rho$ contribution into the Parsafar−Mason theory. As discussed above, the importance of this term might mainly depend on the balance between repulsive and attractive forces, which varies depending on the material and is only indirectly related to the interaction (correlation) range in a particular substance. At present, we cannot distinguish between these possible explanations, and of course, either or both might apply, depending on the material. We note that for all solids considered, including neon, the $|g/f|$ ratio is small, indicating that the $1/\rho$ contribution is important in EoS III.

It is also instructive to compare ratios of corresponding coefficients (same powers in density) in EoS III, EoS II, and EoS I. The relevant ratios are b/g to compare EoS III and EoS I and d/f to compare EoS III and EoS II. If b/g is near 1, then the $1/\rho$ term in EoS III is unimportant, and EoS I will be an accurate equation of state. If d/f is near 1, then the $1/\rho$ term dominates, and EoS II will apply. These ratios are given for some substances in Table 9, and we see that, consistent with the above discussion, b/g is nearest 1 for relatively simple nonpolar liquids, and d/f is nearest 1 for metallic and ionic solids. Results for fluid neon are not given because the data cannot be fitted even "approximately" by EoS I or EoS II.

VII. Summary and Conclusion

In this paper, we suggest an equation of state that gives highly accurate fits to pvT data for a wide variety of materials over a great range of conditions, some of which could be considered extreme. We call this new equation of state EoS III because it builds on earlier linear regularities (EoS I[10] and EoS II[11]) that perform well for particular materials. EoS I works well for many materials composed of relatively simple nonpolar molecules, and EoS II was "designed" specifically for liquid metals such as cesium. EoS III is not a linear regularity because it contains two density-dependent terms, but with just three temperature-dependent parameters, it appears to work very well for fluids and solids of any type. EoS III will be particularly useful in cases where both EoS I and EoS II prove inadequate. For example, Alavi[52] has reported that experimental pvT data of water show a systematic deviation from the linear prediction of EoS I over a large pressure range at 298 K. EoS III fits the same experimental data[36] with $R^2 = 0.99999$. Also, long-chain hydrocarbons show significant deviation from linearity for EoS I,[19,20] but again, EoS III fits this data with $R^2 = 1.000$.

EoS III is based on an effective near-neighbor pair potential of the ELJ(12,6,3) type. This is more general than the LJ(12,6) and Mie(6,3) forms used in EoS I and EoS II, respectively. This introduces one additional temperature-dependent parameter into EoS III, giving three adjustable parameters in total. We also allow the coefficients of the ELJ(12,6,3) potential to be temperature-dependent, again a generalization of EoS I and EoS II. This means that the parameters in EoS III have a more complicated temperature dependence than those of EoS I and EoS II. We give general expressions for this temperature dependence and show that they give a good representation of available data for nitrogen.

In EoS III, the terms in the effective near-neighbor pair potential are related to corresponding terms in the equation of

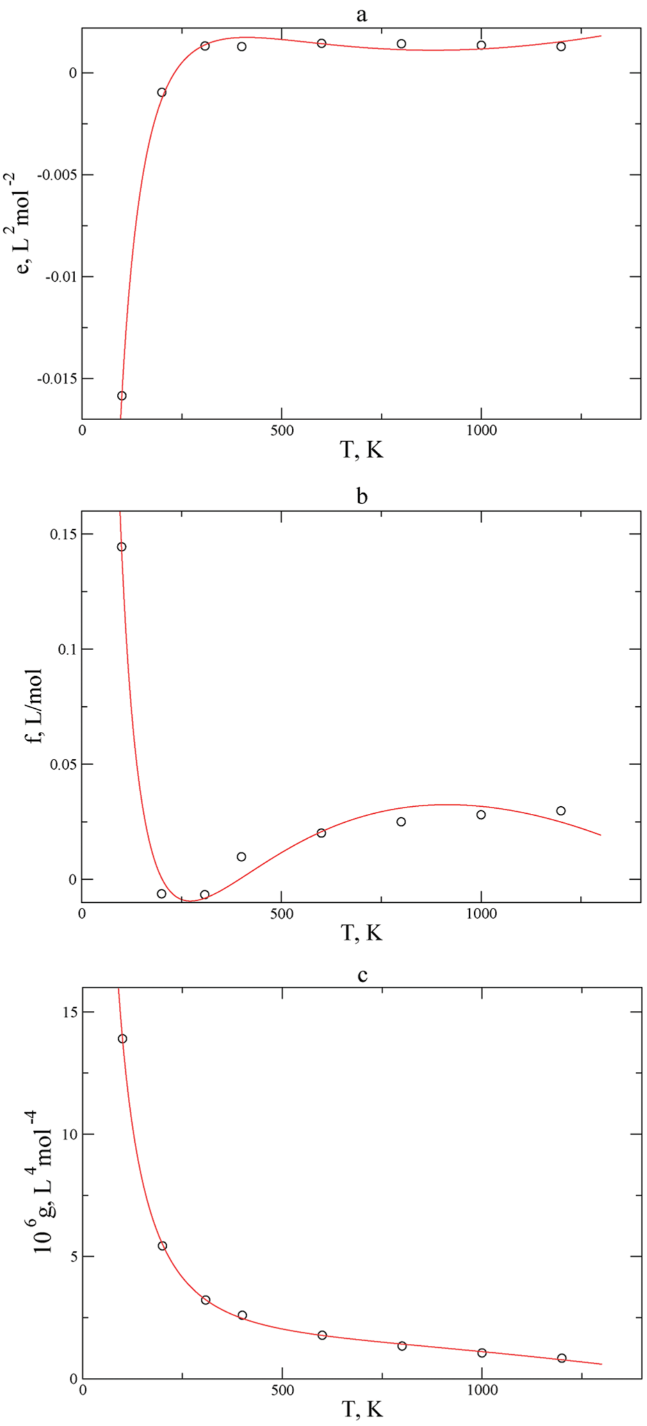

Figure 7. Fitting the parameters of EoS III for nitrogen to eqs 20a−20c. The parameter e is shown in (a), f in (b), and g in (c).

state. Therefore, we have attempted to understand the possible physical significance of the different contributions to the effective potential by comparing the relative magnitudes of parameters in EoS III for different materials. This analysis indicates that the $1/\rho$ term in EoS III is particularly important in systems where long-range correlations are expected, such as polar, ionic, and metallic fluids and solids. This term in EoS III is related to the r^{-3} contribution in the effective potential. Thus, one is tempted to speculate that including this term allows the effective near-neighbor model sufficient flexibility to account for the influence of long-range effects on the equation of state. However, we have found that the $1/\rho$ term is essential to fit experimental data for supercritical neon, for which results are available over a wide range of densities. It is also necessary to describe solid neon. Since there are no obvious long-range interactions or correlations in fluid neon, the neon results suggest that the above explanation is at best incomplete.

TABLE 9: Significance of the Different Terms in Equation 9[a]

substance	T, K	$10^4 \times |g/f|$, (L/mol)^3	b/g	d/f
n-$C_{19}H_{40}$	343.15	428	0.533	
n-C_9H_{20}	303.15	59.6	0.665	
Ar	308.15	16.2	0.986	
C_3H_8	308.15	11.9	0.919	
N_2	308.15	4.86	1.03	
CH_4	308.15	4.30	1.05	
CO	308.15	3.38	1.05	
CH_3OH	300	1.50	0.793	
Hg	303	0.0973	0.840	
Ne(fluid)	298	0.0533		
H_2O	298.15	0.0320	1.67	
CsCl	293.15	0.0173	8.73	1.13
$CaCO_3$	300	0.00636		1.08
NaCl	300	0.00344		0.935
Au	300	0.000490		1.15
Ne(solid)	298	0.000216	3.42	1.36
C(diamond)	298	0.0000555	−2.03	0.671

[a] Note that CsCl and all substances listed below it are solids; all above CsCl are fluids.

Searching for another explanation as to why the $1/\rho$ contribution is crucially important for some materials but not at all for others, we noted that at the van der Waals level, the coefficient of the $1/\rho$ term in the expansion of $(Z - 1)v^2$ contains opposing contributions from the repulsive and attractive parts of the intermolecular force. If these contributions cancel exactly, then the term vanishes; if they do not cancel exactly, the $1/\rho$ term will contribute, and its magnitude will depend on the extent of the cancellation. For neon, the dispersion interaction is considerably weaker than that for argon, which might reduce the cancellation and explain why EoS I is excellent for argon but fails completely for neon. Now, while it is obvious that the van der Waals expression is not valid for dense fluids and solids, it is possible that a similar cancellation, or lack thereof, also controls the importance of the $1/\rho$ term in dense materials. Such an effect would be only indirectly related to the range of the interactions and correlations in a particular system. Of course, these possible explanations of the relevance of the r^{-3} term are not mutually exclusive, and either or both might apply, depending on the material.

We are applying MD simulations together with experimental results to examine the validity of EoS III for ionic liquids, where both short- and long-range interactions are important.[23] Molecular dynamics results for one model ionic liquid are given in this paper and serve to show that EoS III is excellent for these systems, whereas both EoS I and EoS II are not adequate. An advantage of the MD approach is that the internal and nonideal thermal pressure contributions to the equation of state can be separated. For model ionic liquids, we find that both contributions are of comparable magnitude and have a similarly strong dependence on density. This contrasts with the situation for simpler systems such as argon, where the density dependence of the nonideal thermal pressure contribution is relatively weak.[10] Our calculations show that the argon observations cannot be generalized to more complex systems and that, in general, one must expect the coefficients of EoS III (and also those of EoS I and EoS II) to contain contributions from both terms in the exact thermodynamic equation of state. If the internal and thermal pressure contributions cannot be separated, this further complicates any attempt to relate these coefficients to the underlying intermolecular forces.

Acknowledgment. G. A. Parsafar acknowledges The Sharif University of Technology for the financial support during his sabbatical leave at UBC. The financial support of the Natural Science and Engineering Research Council of Canada is gratefully acknowledged. This research has been enabled by the use of WestGrid computing resources, which are funded in part by the Canada Foundation for Innovation, Alberta Innovation and Science, BC Advanced Education, and the participating research institutions. WestGrid equipment is provided by IBM, Hewlett−Packard, and SGI.

References and Notes

(1) Macdonald, J. R. *Rev. Mod. Phys.* **1969**, *41*, 316.

(2) Staccy, F. D.; Brennan, B. J.; Irrvine, R. D. *Geophys. Surv.* **1981**, *4*, 189.

(3) Holzapfel, W. B. *Phys. Rev. B* **2003**, *67*, 026102.

(4) Kumari, M.; Dass, N. *J. Phys.: Condens. Matter* **1990**, *2*, 3219.

(5) Baonza, V. G.; Caceres, M.; Nunez, J. *J. Phys. Chem.* **1994**, *98*, 4955.

(6) Jiuxum, S. *J. Phys.: Condens. Matter* **2005**, *17*, L103.

(7) Vinet, P.; Smith, J. R.; Ferrante, J.; Rose, J. H. *Phys. Rev. B* **1987**, *35*, 1945.

(8) Parsafar, G. A.; Farzi, N.; Najafi, B. *Int. J. Thermophys.* **1997**, *18*, 1197.

(9) Parsafar, G. A.; Mason, E. A. *Phys. Rev. B* **1994**, *49*, 3049.

(10) Parsafar, G. A.; Mason, E. A. *J. Phys. Chem.* **1993**, *97*, 9048.

(11) Ghatee, M. H.; Bahadori, M. *J. Phys. Chem. B* **2001**, *105*, 11256.

(12) Shokouhi, M.; Parsafar, G. A.; Dinpajooh, M. *Fluid Phase Equilib.* **2008**, *271*, 94.

(13) Xu, J.; Herschbach, D. R. *J. Phys. Chem.* **1992**, *96*, 2307.

(14) Huang, Y.-H.; O'Connell, J. P. *Fluid Phase. Equilib.* **1987**, *37*, 75.

(15) Parsafar, G. A.; Kermanpour, F.; Najafi, B. *J. Phys. Chem. B* **1999**, *103*, 7287.

(16) Rose, J. H.; Smith, J. R.; Guinea, F.; Ferrante, J. *J. Phys. Rev. B* **1984**, *29*, 2963.

(17) Najafi, B.; Parsafar, G. A.; Alavi, S. *J. Phys. Chem.* **1995**, *99*, 9248.

(18) Alavi, S.; Parsafar, G. A.; Najafi, B. *Int. J. Thermophys.* **1995**, *16*, 1421.

(19) Parsafar, G. A.; Kalantar, Z. *Iran. J. Chem. Chem. Eng.* **2003**, *22*, 1.

(20) Parsafar, G. A.; Kalantar, Z. *Fluid Phase Equilib.* **2005**, *234*, 11.

(21) Keshavarzi, E.; Parsafar, G. A. *J. Phys. Chem. B* **1999**, *104*, 6584.

(22) Winter, R.; Hensel, F.; Bodensteiner, T.; Glaeser, W. *J. Phys. Chem.* **1988**, *92*, 7171.

(23) Parsafar, G. A.; Spohr, H. V.; Patey, G. N. To be published.

(24) Parsafar, G. A.; Mason, E. A. *J. Phys. Chem.* **1994**, *98*, 1962.

(25) Robertson, S. L.; Babb, S. E., Jr. *J. Chem. Phys.* **1970**, *53*, 1094.

(26) Robertson, S. L. *J. Chem. Phys.* **1993**, *99*, 9322.

(27) Setzmann, U.; Wagner, W. *J. Phys. Chem. Ref. Data* **1991**, *20*, 1061.

(28) Jacobsen, R. T.; Stewart, R. B.; Jahangiri, M. *J. Phys. Chem. Ref. Data* **1986**, *15*, 735.

(29) Robertson, S. L.; Babb, S. E., Jr. *J. Chem. Phys.* **1969**, *50*, 4560.

(30) Stewart, R. B.; Jacobsen, R. T. *J. Phys. Chem. Ref. Data* **1989**, *18*, 639.

(31) Robertson, S. L.; Babb, S. E., Jr.; Scott, G. J. *J. Chem. Phys.* **1969**, *50*, 2160.

(32) Robertson, S. L.; Babb, S. E., Jr. *J. Chem. Phys.* **1969**, *51*, 1357.

(33) Grindley, T.; Lind, J. E., Jr. *J. Chem. Phys.* **1978**, *68*, 5046.

(34) Dutour, S.; Daridon, J. L.; Lagourette, B. *Int. J. Thermophys.* **2000**, *21*, 173.

(35) Goodwin, R. D. *J. Phys. Chem. Ref. Data* **1987**, *16*, 799.

(36) Grindley, T.; Lind, J. E., Jr. *J. Chem. Phys.* **1971**, *54*, 3983.

(37) Eggenberger, R.; Gerber, S.; Huber, H.; Searles, D.; Welker, M. *J. Chem. Phys.* **1993**, *99*, 9163.

(38) Heinz, D. L.; Jeanloz, R. *J. Appl. Phys.* **1984**, *55*, 885.

(39) Dewaele, A.; Datchi, F.; Loubeyre, P.; Mezouar, M. *Phys. Rev. B* **2008**, *77*, 094106-1.

(40) Stewart, J. W. *J. Phys. Chem. Solids* **1956**, *1*, 146.

(41) Kesselman, P. M.; Bykov, A. Yu.; Inshakov, S. A. *J. Eng. Phys. Thermophys.* **1991**, *59*, 1455.

(42) Matsui, M. *Phys. Earth Planet. Inter.* **2009**, *174*, 93.

(43) Perez-Albuerne, E. A.; Drickamer, H. G. *J. Chem. Phys.* **1965**, *43*, 1381.

(44) Akbarzadeh, H.; Shokouhi, M.; Parsafar, G. A. *Mol. Phys.* **2008**, *106*, 2545.

(45) Feistel, R.; Wagner, W. *J. Phys. Chem. Ref. Data* **2006**, *35*, 1021.

(46) Mammone, J. F.; Mao, H. K.; Bell, P. M. *Geophys. Res. Lett.* **1981**, *8*, 140.

(47) Jeanloz, R.; Rudy, A. *J. Geophy. Research* **1987**, *92*, 11433.

(48) Anderson, M. S.; Swenson, C. A. *J. Phys. Chem. Solids* **1975**, *36*, 145.

(49) Anderson, M. S.; Swenson, C. A. *Phys. Rev. B* **1974**, *10*, 5184.

(50) Wanner, R.; Meyer, H. *J. Low Temp. Phys.* **1973**, *11*, 715.

(51) Taravillo, M.; Baonza, V. G.; Nunez, J.; Caceres, M. *Phys. Rev. B* **1996**, *54*, 7034.

(52) Alavi, S. *Int. J. Thermophys.* **1997**, *18*, 1035.

JP903519C