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# Equation of State for Compressed Liquids from Surface Tension

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A method for predicting an analytical equation of state for liquids from the surface tension and the liquid density at the freezing temperature ($\gamma_f, \rho_f$) as scaling constants is presented. The reference temperature, $T_{ref}$, is introduced and the product ($T_{ref}T_f^{1/2}$) is shown to be an advantageous corresponding temperature for the second virial coefficients, $B_2(T)$, of spherical and molecular fluids. Thus, $B_2(T)$ follows a promising corresponding-states principle and then calculations for $\alpha(T)$ and $b(T)$, the two other temperature-dependent constants of the equation of state, are made possible by scaling. As a result, ($\gamma_f, \rho_f$) are sufficient for the determination of thermophysical properties of fluids from the freezing line up to the critical temperature. The present procedure has the advantage that it can also be used in cases where $T_c$ and $P_c$ are not known or the vapor pressure is too small to allow accurate measurements. We applied the procedure to predict the density of Lennard-Jones liquids over an extensive range of temperatures and pressures. The results for liquids with a wide range of acentric factor values are within 5%.

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**KEY WORDS:** compressed liquids; corresponding states; equation of state; surface tension.

## 1. INTRODUCTION

The equation of state is the most fundamental equation in providing a basis for accurate thermophysical properties. Efforts have been made to make progress in this field on both an empirical and a statistical mechanical basis, although the wide ranges of the type of intermolecular potentials that are associated with the different systems leave many unsolved

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problems. The applicability of an equation of state to a given system is reliable if, in the first place, accurate input data are available. In practice, the input data may not be available for a given system or it may not be possible to measure these data accurately for some systems. Hence, there is a need to extend the method by using alternative procedures.

In recent works, we have demonstrated that the cohesive energy density and the density at triple point are sufficient to predict thermophysical properties of compressed normal liquids [1], their mixtures [2], and molten alkali metals [3]. The input data here are used to calculate the temperature-dependent constants, $B_2(T)$, $\alpha(T)$, and $b(T)$, of the statistical mechanical equation of state derived by Song et al. [4]. $B_2(T)$, the second virial coefficient, is calculated from a corresponding-states correlation for the normal liquids. Both $\alpha(T)$, which is the contributton of the repulsive side of the potential function to the second virial coefficien, and $b(T)$, which is the analogue of the van der Waals covolume, can be calculated by integration. This requires the pair potential function to be known. However, $\alpha(T)$ and $b(T)$ can also be calculated from the second virial coefficient by scaling. Therefore, the second virial coefficient can be used to characterize the entire equation of state, over the entire range of temperatures and pressures. All the parameters plus a free parameter of the equation of state, $\Gamma$, that is to be determined by iteration, characterize a particular system for thermophysical properties from the freezing line up to the critical temperature.

Therefore, the second virial coefficient is the central quantity in the treatment of the equation of state. Theoretically, it can be calculated from the pair potential function [5] and the radial distribution function in the gaseous state. It is interesting to see that, among the thermodynamic functions that can be measured directly, the surface energy, $E_s$ can also be calculated from the same information [6, 7]. Determination of the radial distribution function is not an easy task. However, since $B_2(T)$ and $E_s$ use the same parametric function, a correlation can be constructed between them. This is well justified because both $B_2(T)$ and $E_s$ represent the structure and the associated interaction through the radial distribution function and the potential function, respectively. Thus, an alternative procedure to apply the statistical–mechanical equation of state to normal fluids is to take an energy function like the surface energy that is closely related to the intermolecular potential of the system at a reference point. The reduced form of this function can then be used in a corresponding-states correlation for second virial coefficient. Specifically, as we show in the next section, the equation of state involves a corresponding-states principle. As the nature of the alternative procedure implies, the corresponding states principle retains its value.

The purpose of this paper is to present a method for predicting the equation of state of a compressed liquid from properties that are readily available at ordinary pressure and temperature. In particular, we use the surface tension and the liquid density at the triple point as two parameters that can correlate and predict the behavior of compressed liquids. However, the problem we wish to consider here involves predictions for liquids for which $T_c$ and $P_c$ are not known or the vapor pressure is too small, either because they have not been measured or because the liquids decompose at high temperatures.

## 2. THEORETICAL BACKGROUND

We consider the statistical–mechanical equation of state derived by Song and Mason [4], which is based on the Week–Chandler–Anderson (WCA) perturbation theory for the condensed state. The derivation begins with the equation relating the pressure to the pair distribution function, $g(r)$,

$$P/\rho kT = 1 - (2\pi\rho/3kT) \int_0^\infty [\partial u/\partial r)\, g(r)\, r^3\, dr \tag{1}$$

where $P$ is the pressure, $\rho$ is the density, $kT$ is the thermal energy per molecule, and $\partial u/\partial r$ is the derivative of the intermolecular potential function with respect to the distance $r$. Upon applying the perturbation scheme of the WCA method to the potential function and working out a correction for attractive forces, the equation of state reads

$$P/\rho kT = 1 - [(\alpha - B_2)\,\rho/(1 + 0.22\Gamma b\rho)] + \alpha\rho G(b\rho) \tag{2}$$

where the new corresponding-states principle has the form

$$G(b\rho)^{-1} = \{(1/\alpha\rho)[Z - 1 + (\alpha - B_2)\,\rho/(1 + 0.22\Gamma b\rho)]\}^{-1} \approx (1 - \Gamma b\rho) \tag{3}$$

and $Z = P/\rho kT$ is the compressibility factor. Here $G(b\rho)$ is the average pair distribution function at contact for equivalent hard convex bodies that still have the pairwise additivity of the intermolecular forces as in $g(r)$. The many-body nature of the system may be contained in $G(b\rho)$ [8]. The value of $B_2$ can be calculated by integration if the form of potential function is known. $\alpha$ is the contribution of the repulsive side of the potential function to the second virial coefficient and it takes care of the softness of the potential function. $b$ is the analogue of van der Waals covolume. Both $\alpha(T)$, and $b(T)$ can be calculated by integration if the potential function is known. $G(b\rho)^{-1}$ is a function of $b\rho$ only and satisfies corresponding states, varying linearly with slope $\Gamma$ over the whole range of temperatures from the freezing line up to the critical point. The functional form of $G(b\rho)^{-1}$ implies that, according to corresponding states, all the $P$–$V$–$T$ data collapse to a single line. The value of $\Gamma$, determined from $P$–$V$–$T$ data by iteration, along with $B_2(T)$, $\alpha(T)$, and $b(T)$, characterizes the thermodynamic properties of particular systems.

According to Eq. (2), knowing the form of the potential function, the thermophysical properties of both spherical and nonspherical fluids can be characterized over the entire range of temperatures including compressed liquids. The form of Lennard–Jones (12–6) potential function reproduces thermophysical properties within experimental uncertainty [8]. More accurate potential functions based on the Hartree–Fock–Dispersion interaction potential are also available [8]. However, it is not the purpose of this paper to use any of these functions. Rather, it will be shown that the idea of minimal as well as practical input data of the analytical equation of state can be extended nicely to include other thermodynamic function, e.g., the surface energy.

## 3. CORRELATION PROCEDURE

The method we follow here is to use an energy function involving the surface tension as a scaling constant for the calculation of the temperature-dependent constants, $B_2(T)$, $\alpha(T)$, and $b(T)$, in Eq. (2). This is based on the fact that the surface tension is a measure of the cohesive energy density and that the ranges of the effective forces are not larger than the molecular dimension [9, 10]. A suitable form of the energy function is $\gamma\rho^{-2/3}N^{1/3}$, where $\gamma$ is the surface tension, $\rho$ is the molar liquid density, and $N$ is Avogadro's number. Compared with thermal energy, the reduced form of the function, with the triple point as a reference temperature, takes the form $\gamma_{\mathrm{tr}}\rho_{\mathrm{tr}}^{-2/3}N^{1/3}/RT$. The term $\gamma_{\mathrm{tr}}\rho_{\mathrm{tr}}^{-2/3}N^{1/3}/R$ is referred to as $T_{\mathrm{ref}}$. It should be emphasized that the reference temperature is not an essential choice, but merely a convenient one. Our final correlation scheme is self-correcting the normal freezing temperature would probably work as well. Apparently the *shape* effects described by $\omega$, the acentric factor, affect the $\gamma_{\mathrm{tr}}$ and $\rho_{\mathrm{tr}}$ (often approximated by $\rho_{\mathrm{f}}$) in such a way as to tend to compensate for their influence on $B_2(T)$.

For a number of gases and liquids ranging from simple gases such as neon and argon to more complex liquids such as octane and toluene, we tried to relate $B_2^*(T)$ $(=\rho_{\mathrm{f}} B_2(T))$ to $T_{\mathrm{ref}}$, with the intention of obtaining a corresponding-states correlation. As was indicated by large number of scattered data point particularly at low temperatures, we concluded that $T_{\mathrm{ref}}$ fails to be such a corresponding temperature quantity for $B_2^*(T)$. The way that scattering among the fluids occurs indicated that, for our purpose, another parameter corresponding to the nature of each fluid has to be coupled with $T_{\mathrm{ref}}$.

Here it is proposed that the freezing temperature, $T_{\mathrm{f}}$, which was shown to be a corresponding temperature for different substances [11], is a suitable choice. This choice can be further justified by noting that $T_{\mathrm{ref}}$ contains the surface tension and the liquid density at the freezing temperature. In other words, for different liquids $T_{\mathrm{ref}}$ and $T_{\mathrm{f}}$ are readily available. Empirically we found that the product $(T_{\mathrm{ref}} T_{\mathrm{f}}^{1/2})$ is an excellent characteristic corresponding temperature for both the spherical and the molecular liquids. Therefore, the corresponding-states correlation for $B_2^*(T)$ in terms of the two scaling constants can be represented by

$$B_2^*(T) = 0.0804 - 2.1288T^{*-1} - 8.5597T^{*-2} + 7.4294T^{*-3} - 3.3494T^{*-4} \tag{4}$$

where

$$T^* = [TT^{1/2}/T_{\mathrm{ref}} T_{\mathrm{f}}^{1/2}]^{3/4} \tag{5}$$

We used the tabulations of Dymond and Smith [12], Vargaftik [13], and Adamson [7] for the second virial coefficients, liquid densities, and surface tensions, respectively, to construct the correlation, Eq. (4), shown

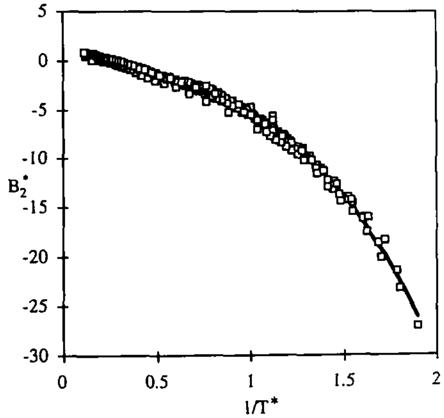

**Fig. 1.** $B_2^*$, $\rho_{\mathrm{f}} B_2(T)$, versus $1/T^*$ for methane, ethane, propane, butane, pentane, hexane, heptane, octane, benzene, nitrogen, neon, and argon. Due to extensive overlap of the experimental data, the same marker (square) was used. The solid line represents the polynomial fit.

in Fig. 1. As can be seen, there is a strong correlation for all fluids considered over the entire range of temperature. It should be mentioned that $T^*$ is original and is responsible for a promising correlation, allowing the second virial coefficient to be calculated accurately.

For Lennard–Jones fluids, Song and Mason [14] have obtained relationships that allow the calculation of $\alpha(T)$ and $b(T)$, taking into account that they depend only slightly on the details of the shape of the potential function. In practice, this requires Eq. (4) to be solved for the reduced Boyle's temperature and the reduced Boyle's volume, so that

$$\rho_f \alpha = a_1[\exp(-c_1 T^*)] + a_2[1-\exp(-c_2/T^{*1/4})] \tag{6}$$

and

$$\begin{aligned} \rho_f b = {} & a_1[(1-c_1 T^*)\exp(-c_1 T^*)] \\ & + a_2[1-(1+0.25c_2/T^{*1/4})\exp(-c_2/T^{*1/4})] \end{aligned} \tag{7}$$

where

$$\begin{aligned} a_1 &= -0.01054, \qquad & c_1 &= 0.7613 \\ a_2 &= 2.9387, \qquad & c_2 &= 1.3227 \end{aligned} \tag{8}$$

The characteristic free parameter of the fluids in the equation of state, $\Gamma$, can be calculated from the two scaling constants at freezing temperature ($\gamma_f$ and $\rho_f$) in a single iteration because it is just a correction factor.

## 4. RESULTS AND DISCUSSION

The cohesive energy density can be represented by both the heats of vaporization and the surface energy. It would be attractive to correlate the heat of vaporization with the surface tension and then use the data from our previous work [1, 2], but we noticed that the correlation is poor. This observation is in accord with the fact that lattice theories are now regarded as a rather unsuccessful chapter in the history of liquids [15].

In Eq. (4), the term $(T/T_f)^{1/2}$ reduces the scattering among the fluids with a wide range of acentric factors from Ne and Ar ($\omega = 0$) to octane ($\omega = 0.394$). Therefore, this term is mainly responsible for the accurate value prediction of the second virial coefficient, without which no principle of corresponding states of moderate accuracy existed even for spherical liquids over the appreciable range of temperature. $T^{*4/3}$ makes a corresponding states correlation quite well, but $T^*$ finds the best fit to Eq. (4). We took a large number of data (277 data points) to prevent any oscillations due to the high degree of the polynomial, e.g., Eq. (4).

Table I. Density of the Liquid State of Fluids at Saturation Pressures[a]

| $T$ (K) | $P$ (bar)[b] | $\rho_{\text{calc}}$ (mol · L$^{-1}$) | $\rho_{\text{expt}}$ (mol · L$^{-1}$) | Dev. (%)[c] |
|---|---|---|---|---|
| | | $C_8H_{18}$ | | |
| 253.15 | 7.907 (−4) | 6.179 | 6.431 | −4.079 |
| 263.15 | 1.800 (−3) | 6.153 | 6.360 | −3.365 |
| 273.15 | 3.813 (−3) | 6.121 | 6.289 | −2.751 |
| 283.15 | 7.507 (−3) | 6.084 | 6.219 | −2.214 |
| 293.15 | 1.395 (−2) | 6.042 | 6.148 | −1.755 |
| 303.15 | 2.460 (−2) | 5.995 | 6.077 | −1.369 |
| 313.15 | 4.147 (−2) | 5.945 | 6.006 | −1.021 |
| 323.15 | 6.713 (−2) | 5.891 | 5.934 | −0.725 |
| 333.15 | 1.049 (−1) | 5.833 | 5.861 | −0.479 |
| 343.15 | 1.587 (−1) | 5.774 | 5.787 | −0.230 |
| 353.15 | 2.334 (−1) | 5.712 | 5.712 | −0.008 |
| 363.15 | 3.345 (−1) | 5.649 | 5.636 | 0.223 |
| 373.15 | 4.683 (−1) | 5.584 | 5.559 | 0.450 |
| 383.15 | 6.420 (−1) | 5.517 | 5.480 | 0.676 |
| 393.15 | 8.635 (−1) | 5.450 | 5.399 | 0.940 |
| 403.15 | 1.141 (00) | 5.382 | 5.316 | 1.229 |
| 413.15 | 1.484 (00) | 5.314 | 5.231 | 1.566 |
| 423.15 | 1.902 (00) | 5.244 | 5.143 | 1.918 |
| 433.15 | 2.406 (00) | 5.174 | 5.054 | 2.327 |
| | | $C_6H_5\text{-}CH_3$ | | |
| 223.15 | 1.387 (−4) | 9.759 | 10.114 | −3.633 |
| 233.15 | 3.853 (−4) | 9.746 | 10.013 | −2.735 |
| 243.15 | 9.600 (−4) | 9.724 | 9.912 | −1.930 |
| 253.15 | 2.173 (−3) | 9.691 | 9.811 | −1.235 |
| 263.15 | 4.573 (−3) | 9.649 | 9.711 | −0.641 |
| 273.15 | 8.960 (−3) | 9.597 | 9.611 | −0.146 |
| 283.15 | 1.673 (−2) | 9.537 | 9.510 | 0.282 |
| 293.15 | 2.912 (−2) | 9.469 | 9.409 | 0.632 |
| 303.15 | 4.889 (−2) | 9.394 | 9.308 | 0.914 |
| 313.15 | 7.888 (−2) | 9.313 | 9.207 | 1.136 |
| 323.15 | 1.228 (−1) | 9.226 | 9.104 | 1.321 |
| 333.15 | 1.852 (−1) | 9.135 | 9.001 | 1.467 |
| 343.15 | 2.716 (−1) | 9.040 | 8.897 | 1.584 |
| 353.15 | 3.883 (−1) | 8.942 | 8.790 | 1.695 |
| 363.15 | 5.423 (−1) | 8.841 | 8.683 | 1.787 |
| 373.15 | 7.417 (−1) | 8.737 | 8.574 | 1.860 |
| 383.15 | 9.955 (−1) | 8.632 | 8.464 | 1.949 |
| 393.15 | 1.312 (00) | 8.526 | 8.355 | 2.005 |
| 403.15 | 1.704 (00) | 8.418 | 8.246 | 2.039 |
| 413.15 | 2.180 (00) | 8.309 | 8.138 | 2.063 |
| 423.15 | 2.752 (00) | 8.199 | 8.029 | 2.075 |
| 433.15 | 3.433 (00) | 8.087 | 7.811 | 3.407 |

[a] The results of the same calculations for all the substances in Table III are better than 5%.

[b] The values in parentheses are the powers of 10.

[c] The percentage deviations calculated before the densities have been rounded off.

Table I. *(Continued)*

| $T$ (K) | $P$ (bar)[b] | $\rho_{calc}$ ($mol \cdot L^{-1}$) | $\rho_{expt}$ ($mol \cdot L^{-1}$) | Dev. (%)[c] |
|---|---|---|---|---|
| | | Xe | | |
| 163 | 8.998 (−1) | 22.687 | 22.635 | 0.228 |
| 164 | 9.546 (−1) | 22.617 | 22.574 | 0.189 |
| 166 | 1.071 (00) | 22.478 | 22.452 | 0.114 |
| 168 | 1.199 (00) | 22.339 | 22.331 | 0.038 |
| 170 | 1.337 (00) | 22.199 | 22.216 | −0.078 |
| 172 | 1.488 (00) | 22.059 | 22.102 | −0.195 |
| 174 | 1.651 (00) | 21.918 | 21.980 | −0.284 |
| 176 | 1.827 (00) | 21.777 | 21.866 | −0.408 |
| 178 | 2.017 (00) | 21.636 | 21.759 | −0.570 |
| 180 | 2.222 (00) | 21.494 | 21.637 | −0.667 |
| 184 | 2.678 (00) | 21.210 | 21.417 | −0.974 |
| 188 | 3.200 (00) | 20.923 | 21.188 | −1.267 |
| 192 | 3.794 (00) | 20.635 | 20.967 | −1.610 |
| 196 | 4.465 (00) | 20.344 | 20.754 | −2.015 |
| 200 | 5.220 (00) | 20.051 | 20.526 | −2.367 |
| 204 | 6.064 (00) | 19.754 | 20.289 | −2.710 |
| 208 | 7.004 (00) | 19.453 | 20.069 | −3.164 |
| 212 | 8.045 (00) | 19.149 | 19.840 | −3.609 |
| 216 | 9.194 (00) | 18.840 | 19.596 | −4.015 |
| 220 | 1.046 (+1) | 18.526 | 19.345 | −4.421 |

Table II. Density of the Liquid State of Fluids at High Pressures[a,b]

| $T$ (K) | $P$ (bar) | $\rho_{calc}$ ($mol \cdot L^{-1}$) | $\rho_{expt}$ ($mol \cdot L^{-1}$) | Dev. (%)[c] |
|---|---|---|---|---|
| | | $C_8H_{18}$ | | |
| 373.15 | 20 | 5.597 | 5.608 | −0.204 |
| | 30 | 5.604 | 5.626 | −0.400 |
| | 40 | 5.611 | 5.641 | −0.533 |
| | 50 | 5.618 | 5.656 | −0.668 |
| | 60 | 5.625 | 5.670 | −0.803 |
| | 70 | 5.631 | 5.685 | −0.957 |
| | 80 | 5.637 | 5.696 | −1.046 |
| | 90 | 5.644 | 5.711 | −1.184 |
| | 100 | 5.650 | 5.726 | −1.341 |
| | 120 | 5.662 | 5.748 | −1.525 |
| | 140 | 5.674 | 5.775 | −1.778 |
| | 160 | 5.686 | 5.794 | −1.899 |
| | 180 | 5.697 | 5.817 | −2.108 |
| | 200 | 5.708 | 5.836 | −2.251 |

[a] To cover the whole range, some results for low pressures inserted.

[b] The results of the same calculations for all the substances in Table III are better than 5%.

[c] The percentage deviations calculated before the densities have been rounded off.

Table II. *(Continued)*

| $T$ (K) | $P$ (bar) | $\rho_{calc}$ $(mol \cdot L^{-1})$ | $\rho_{expt}$ $(mol \cdot L^{-1})$ | Dev. (%)$^c$ |
|---|---|---|---|---|
| 413.15 | 20 | 5.335 | 5.283 | 0.966 |
| | 30 | 5.347 | 5.306 | 0.769 |
| | 40 | 5.358 | 5.329 | 0.551 |
| | 50 | 5.369 | 5.348 | 0.391 |
| | 60 | 5.379 | 5.368 | 0.210 |
| | 70 | 5.390 | 5.384 | 0.107 |
| | 80 | 5.400 | 5.404 | −0.077 |
| | 90 | 5.410 | 5.418 | −0.139 |
| | 100 | 5.420 | 5.434 | −0.265 |
| | 120 | 5.439 | 5.465 | −0.476 |
| | 140 | 5.457 | 5.496 | −0.710 |
| | 160 | 5.475 | 5.523 | −0.886 |
| | 180 | 5.492 | 5.548 | −1.019 |
| | 200 | 5.508 | 5.569 | −1.110 |
| 453.15 | 20 | 5.062 | 4.927 | 2.673 |
| | 30 | 5.079 | 4.960 | 2.339 |
| | 40 | 5.096 | 4.991 | 2.055 |
| | 50 | 5.112 | 5.017 | 1.858 |
| | 60 | 5.128 | 5.043 | 1.657 |
| | 70 | 5.144 | 5.069 | 1.452 |
| | 80 | 5.159 | 5.093 | 1.281 |
| | 90 | 5.173 | 5.117 | 1.088 |
| | 100 | 5.187 | 5.141 | 0.891 |
| | 120 | 5.215 | 5.180 | 0.665 |
| | 140 | 5.241 | 5.220 | 0.392 |
| | 160 | 5.266 | 5.255 | 0.210 |
| | 180 | 5.289 | 5.287 | 0.044 |
| | 200 | 5.312 | 5.316 | −0.067 |
| | | $C_6H_6$ | | |
| 300 | 1 | 11.473 | 11.280 | 1.682 |
| | 10 | 11.477 | 11.280 | 1.717 |
| | 20 | 11.481 | 11.290 | 1.664 |
| | 30 | 11.485 | 11.300 | 1.612 |
| | 40 | 11.489 | 11.310 | 1.559 |
| | 50 | 11.493 | 11.320 | 1.506 |
| | 100 | 11.512 | 11.360 | 1.320 |
| | 200 | 11.549 | 11.472 | 0.666 |
| | 300 | 11.584 | 11.534 | 0.431 |
| | 400 | 11.618 | 11.618 | 0.002 |

**Table II.** *(Continued)*

| $T$ (K) | $P$ (bar) | $\rho_{calc}$ ($mol \cdot L^{-1}$) | $\rho_{expt}$ ($mol \cdot L^{-1}$) | Dev. (%)[c] |
|---|---|---|---|---|
| 350 | 1 | 10.782 | 10.581 | 1.866 |
| | 10 | 10.791 | 10.590 | 1.867 |
| | 20 | 10.799 | 10.607 | 1.777 |
| | 30 | 10.808 | 10.616 | 1.777 |
| | 40 | 10.817 | 10.634 | 1.696 |
| | 50 | 10.825 | 10.642 | 1.687 |
| | 100 | 10.867 | 10.705 | 1.494 |
| | 200 | 10.946 | 10.822 | 1.130 |
| | 300 | 11.018 | 10.933 | 0.770 |
| | 400 | 11.085 | 11.037 | 0.434 |
| 400 | 1 | 0.0310 | 0.0306 | 1.293 |
| | 10 | 10.057 | 9.833 | 2.226 |
| | 20 | 10.073 | 9.856 | 2.155 |
| | 30 | 10.089 | 9.871 | 2.160 |
| | 40 | 10.105 | 9.894 | 2.088 |
| | 50 | 10.121 | 9.909 | 2.092 |
| | 100 | 10.195 | 10.002 | 1.891 |
| | 200 | 10.331 | 10.169 | 1.568 |
| | 300 | 10.451 | 10.325 | 1.207 |
| | 400 | 10.560 | 10.468 | 0.868 |
| | | Xe | | |
| 400 | 10 | 0.308 | 0.307 | 0.273 |
| | 20 | 0.628 | 0.628 | −0.077 |
| | 30 | 0.963 | 0.963 | −0.046 |
| | 40 | 1.313 | 1.315 | −0.176 |
| | 50 | 1.680 | 1.684 | −0.234 |
| | 60 | 2.064 | 2.071 | −0.331 |
| | 70 | 2.466 | 2.477 | −0.437 |
| | 80 | 2.887 | 2.903 | −0.564 |
| | 100 | 3.779 | 3.813 | −0.890 |
| | 150 | 6.158 | 6.324 | −2.703 |
| 500 | 10 | 0.243 | 0.243 | 0.050 |
| | 20 | 0.490 | 0.490 | −0.067 |
| | 30 | 0.742 | 0.742 | −0.047 |
| | 40 | 0.998 | 0.999 | −0.124 |
| | 50 | 1.257 | 1.260 | −0.216 |
| | 60 | 1.521 | 1.525 | −0.247 |
| | 70 | 1.788 | 1.794 | −0.356 |
| | 80 | 2.059 | 2.067 | −0.390 |
| | 100 | 2.608 | 2.623 | −0.575 |
| | 150 | 4.004 | 4.053 | −1.232 |

Table II. *(Continued)*

| $T$ (K) | $P$ (bar) | $\rho_{\text{calc}}$ $(\text{mol} \cdot \text{L}^{-1})$ | $\rho_{\text{expt}}$ $(\text{mol} \cdot \text{L}^{-1})$ | Dev. (%)[c] |
|---|---|---|---|---|
| 600 | 10 | 0.202 | 0.201 | 0.349 |
| | 20 | 0.405 | 0.404 | 0.183 |
| | 30 | 0.609 | 0.609 | 0.052 |
| | 40 | 0.814 | 0.814 | −0.020 |
| | 50 | 1.021 | 1.021 | −0.032 |
| | 60 | 1.228 | 1.230 | −0.163 |
| | 70 | 1.437 | 1.439 | −0.118 |
| | 80 | 1.646 | 1.649 | −0.176 |
| | 100 | 2.065 | 2.071 | −0.282 |
| | 150 | 3.112 | 3.130 | −0.586 |

Table III. Input Data Including $\Gamma$

| Substance | $\gamma_{\text{f}}$ $(\text{J} \cdot \text{m}^{-2})$ | $\rho_{\text{f}}$ $(\text{mol} \cdot \text{m}^{-3})$ | $T_{\text{f}}$ (K) | $\Gamma$ |
|---|---|---|---|---|
| Ne | 0.00590 | 61856.51 | 24.5 | 0.3960 |
| Ar | 0.0132[a] | 35338.78[a] | 83.78 | 0.3970 |
| Kr | 0.0162[b] | 29140.81[b] | 115.76 | 0.3970 |
| Xe | 0.0186[c] | 22635.19[c] | 161.30 | 0.3940 |
| $N_2$ | 0.01217 | 30903.80 | 63.15 | 0.4250 |
| $CH_4$ | 0.01856 | 28257.56 | 90.66 | 0.4408 |
| $C_2H_6$ | 0.03224 | 21909.04 | 89.88 | 0.4801 |
| $C_3H_8$ | 0.03689 | 16640.01 | 85.46 | 0.5034 |
| $n$-$C_4H_{10}$ | 0.03224 | 12391.43 | 134.48 | 0.4810 |
| $n$-$C_5H_{12}$ | 0.03361 | 10552.08 | 143.48 | 0.5016 |
| $n$-$C_6H_{14}$ | 0.03099 | 8781.30 | 177.83 | 0.4940 |
| $n$-$C_7H_{16}$ | 0.03212 | 7719.70 | 182.56 | 0.4950 |
| $n$-$C_8H_{18}$ | 0.02919 | 6709.09 | 216.37 | 0.4960 |
| $C_6H_6$ | 0.03089 | 11554.16 | 278.68 | 0.4321 |
| $C_6H_5$–$CH_3$ | 0.04318 | 10582.32 | 178.16 | 0.4985 |

[a] These values are at 84.3 K.
[b] These values are at 117 K.
[c] These values are at 163 K.

Table I contains the calculated densities for different fluids with a wide range of acentric factors including atomic fluids. Table II contains some results for the liquids at high pressures. We initially calculated the densities for all the compounds in Table III. Only the results for a typical simple and complex liquids are presented. The $P$–$T$ and surface tension data were taken from Refs. 7, 9, and 13. The results for compressed liquids at any pressures and temperatures are better than 5%. This is about the same as the accuracy of the prediction based on constants $T_c$, $P_c$, and $\omega$, the critical temperature and the critical pressure, and the acentric factor, respectively [16]. This indicates that the physical properties can be predicted from just two scaling constants, the surface tension and the liquid density at freezing temperatures, which can readily be measured. Neon shows some deviations, although not appreciably, probably due to the quantum effect.

Our procedure successfully predicts a statistical–mechanical equation of state for simple and complex liquids over a wide range of temperatures and pressures. It should be mentioned that an equation of state plus a functional form of the heat capacity allows the fundamental thermodynamic properties to be determined.

The values of $\Gamma$ for the different fluids are given in Table III. Although it is a characteristic free parameter that incorporates the inaccuracy associated with the temperature-dependent constants too, it is in accordance with the earlier finding of a linear relationship for the corresponding-states function, $G(b\rho)^{-1}$.

In summary, before this work, if experimental values of $B_2(T)$ were not available, one had a choice of using (i) $\varepsilon$ and $r_m$, the potential well depth and position of its minimum, respectively, or (ii) $\Delta H_v$ and $\rho_f$, the heat of vaporization (equivalently cohesive energy [1]) and the density at freezing temperature, respectively, to calculate the temperature dependent constants in Eq. (2). But accurate values of the second virial coefficient are not always available. In, the case that the substance is thermally unstable, to allow the vapor pressures to be determined, the present procedure opens a simple channel to use Eq. (2) for calculating thermophysical properties from just $\gamma_f$ and $\rho_f$.

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