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Equation of State for Complex Liquid Mixtures

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The present work shows a successful extension of previous studies to molecular liquids for which the second virial coefficients are not known. Recent advances in statistical-mechanical theory of equilibrium fluids can be used to obtain an equation of state for compressed liquids. The average contact pair distribution function (G), which is at the heart of the equation of state, has the very simple form of a single curve in $\lambda b^*\rho^*$ (any substance). The effect of many-body forces may still be included in G. The temperature-dependent parameters in the equation can be calculated with reasonable accuracy for most practical purposes just from the experimental heat of vaporization and triple-point density. Thus, thermodynamic consistency is achieved by the use of two scaling parameters (ΔH_ν, ρ_t). In terms of these parameters, the reduced second virial coefficient ($B_2^*(T)$) obeys a single law of corresponding states in which $\alpha^*(T)$ and $b^*(T)$ are only slightly modified. The correlations embrace the temperature range $T_t \leqq T < T_c$ and can be used in a predictive mode. The remaining constant parameters are best found empirically from ρ_t data for pure dense fluids. We tested the equation of state on several liquid mixtures. The results indicate that the density of liquid mixtures can be predicted within about 5% at any pressure and temperature.

Although reliable experimental data are always preferred over values obtained by estimation method, all too often reliable data are not available. The present result is remarkable because the only data used for estimating compressed liquid properties were the density and the heat of vaporization. The Clausius–Clapeyron equation provides a useful method for obtaining the enthalpies of vaporization from more easily measured vapor pressures. Liquid specific volumes are relatively easy to measure, and for most common organic liquids at least one experimental value is available. It should be noted that the accuracy is not necessarily enhanced by greater complexity.

An analytical equation of state, based on statistical-mechanical perturbation theory, has recently been proposed.$^{1)}$ This equation of state is quite accurate over the entire P–ν–T ranges for all nonpolar or slightly polar fluids, including compressed liquids. Three temperature-dependent quantities are needed to use the strong principle: The second virial coefficient ($B_2(T)$), an effective van der Waals covolume ($b(T)$), and a scaling factor ($\alpha(T)$), which is eqivalent to the contribution to $B_2(T)$ from just the repulsive branch of the intermolecular forces. The strong principle may also be characterized by three constants: the Boyle temperature (T_B), the Boyle volume (ν_B), and an empirical constant reflecting the spheracy of the molecule. If the strong principle can be extensively used for molecular liquids, the practical question arises as to how to find the proper scale factors corresponding to T_B, ν_B, and λ in order that the strong principle can have real predictive power. The previous statistical-mechanical theory would take T_B and ν_B from the experimental values of $B_2(T)$, the second virial coefficient of the vapor. However, the values of $B_2(T)$ are hardly known experimentally for many compressed liquids of interest, the present method for finding a suitable scale factor, say, applying the cohesive energy density, would be needed. The present study may be applied to real molecular liquids with no difficulties.

Agreement with measurements has been secured in that the material constants of the different systems and the adjustable constants in the expressions for the functionals have been made consistent with a vast number of experimental results. We recall that knowledge concerning the equation of state combined with that of the specific heat is equivalent to a fundamental equation from which all thermodynamic equilibrium properties can be calculated. An entire P–ν–T surface is collapsed to a single curve; this result appears to hold with remarkable accuracy when tested with experimental data for any number of systems. We tested the equation of state of several liquid mixtures. The results show that the density of the liquid mixtures can be predicted within about 5% at any temperature and pressure.

In short, the purpose of this work was to correlate and to predict the behavior of complex liquid mixtures based on the latent heat of vaporization and the liquid density at the triple point, which are closely related to the cohesive energy density of regular solution theory. An empirical feature is incorporated in the corresponding-states principle, which enables it to describe the thermodynamic properties of mixtures at all liquid densities, temperatures, and compositions.

Equation of State

We omit details concerning the statistical-mechanical perturbation theory derivation which have given elsewhere.$^{2)}$ The equation of state obtained by Ihm, Song, and Mason,$^{1)}$ including a small correction for attractive forces, has the following form:

$$\frac{P}{\rho KT} = 1 - \frac{(\alpha - B_2)}{1 + 0.22\lambda b\rho} + \frac{\alpha\rho}{1 - \lambda b\rho}, \tag{1a}$$

where ρ is the number (molar) density, kT has its usual meaning, and λ is a constant. Three temperature-dependent quantities ($\alpha(T)$, $b(T)$, and $B_2(T)$) are needed to determine the equation of state for a real molecular liquid. The three parameters can be obtained from the internuclear potential ($U(r)$) by integration:

$$B(T) = 2\pi \int_0^\infty \{1 - \exp[-U(r)/kT]\} r^2 \mathrm{d}r, \tag{1b}$$

$$\alpha(T) = 2\pi \int_0^{r_\mathrm{m}} \{1 - \exp[-U_0(r)/kT]\} r^2 \mathrm{d}r, \tag{1c}$$

and

$$b(T) = \alpha + T\frac{\mathrm{d}\alpha}{\mathrm{d}T}. \tag{1d}$$

Here, $U_0(r)$ is the repulsive part of $U(r)$,

$$U_0(r) = \left[\begin{array}{ll} U(r) + \varepsilon, & r < r_\mathrm{m} \\ 0, & r > r_\mathrm{m}, \end{array} \right.$$

where ε is the depth of the potential well and r_m is the position of its minimum. If $U(r)$ is known, it is straight-forward to calculate $B_2(T)$, $\alpha(T)$, and $b(T)$ from Eq. 1b—1d. Such calculations have been carried out by Song et al.[3] for a Lennard–Jones (12,6) potential and for an accurate noble-gas potential. It fortunately turns out that $\alpha(T)$ and $b(T)$ are rather insensitive to the shape of the intermolecular potential, so that they appear nearly universal functions of temperature in terms of a suitable reducing unit, such as the heat of vaporization (ΔH_v) and the triple point density (ρ_t). They are fitted as follows:

$$\alpha\rho_\mathrm{t} = a_1 \exp[-C_1(RT/\Delta H_\mathrm{v})] + a_2\{1 - \exp[-C_2/(RT/\Delta H_\mathrm{v})^{\frac{1}{4}}]\} \tag{2a}$$

and

$$b\rho_\mathrm{t} = a_1[1 - C_1(RT/\Delta H_\mathrm{v})]\exp[-C_1(RT/\Delta H_\mathrm{v})] + a_2\{1 - [1 + \frac{1}{4}C_2(\Delta H_\mathrm{v}/RT)^{\frac{1}{4}})]\exp[-C_2(\Delta H_\mathrm{v}/RT)^{\frac{1}{4}}]\}, \tag{2b}$$

where the constants a_1, a_2, c_1, and c_2 are -0.1053, 2.9359, 5.7862, and 0.7966, respectively.

The central idea is to use second virial-coefficient data to determine the parameters for the corresponding states that are related to the scaling parameters, ΔH_v and ρ_t. The resulting correlation can then be used to calculate $B_2(T)$, which is quite universal. The parameter ΔH_v is determined from the experimental vapor pressure data using the Clausius–Clapeyron equation. It is remarkable that one functional (B_2^*) does suffice for all nonpolar liquids, where, $B_2^* = \rho_\mathrm{t} B(T)$. The values of $B(T)$ are correlated as

$$B_2\rho_\mathrm{t} = 0.4038908 - 0.076485\left(\frac{RT}{\Delta H_\mathrm{v}}\right)^{-2} - 0.0002504\left(\frac{RT}{\Delta H_\mathrm{v}}\right)^{-4}, \tag{2c}$$

where R is the gas constant. This correlation gives good second virial coeficients for different classes of substances up to the critical temperature (T_c).[4] The value of λ can be obtained from Eq. 1a by fitting the ρ_t and ΔH_v data. In summary, the correlation of the second virial coefficients (B_2) requires only the scaling parameters ΔH_v and ρ_t. The values of the parameter ΔH_v were obtained indirectly by calculations based on the results of various vapor pressure measurements.[5] It is important to stress that the present correlation operate in a predictive mode. The second virial coefficient is predicted over a much wider temperature range than that for which direct measurements exist.[6] The $\alpha^*(T)$ and $b^*(T)$ are predicted over a similar wide temperature range, where $\alpha^*(T) = \alpha(T)\rho_\mathrm{t}$ and $b^*(T) = b(T)\rho_\mathrm{t}$.

We can write the corresponding states result in the form

$$\frac{1}{G(b^*\rho^*)} \equiv \alpha^*\rho^*[Z - 1 + \frac{(\alpha^* - B_2^*)\rho^*}{1 + 0.22\lambda b^*\rho^*}]^{-1} = 1 - \lambda b^*\rho^*, \tag{3}$$

where $Z = P/\rho kT$, $\rho^* = \rho/\rho_\mathrm{t}$, and λ is the magnitude of the slope. The fact that λ also occurs on the left-hand side of this euqation means that a successive-approximation procedure is needed to determine its value; usually, however, the triple-point density is sufficient because it is only in a correction term. We now wish to compare the theoretical result from Eq. 1a with the experimental data for molecular liquids. It is convenient to use the average contact pair distribution function (G) defined in Eq. 3. The results for molecular liquids are given in Ref. 4, in terms of G and $\lambda b^*\rho^*$ for any substance represented as a single curve. In other words in the corresponding-states treatment we solve. Eq. 3 for $G(\lambda b^*\rho^*)$, which is then treated as an unknown function to be determined from the experimental P–ν–T data. The result turns out to be surprisingly simple, $G(\lambda b^*\rho^*) \approx (1 - \lambda b^*\rho^*)^{-1}$; that is, a plot of G^{-1} against $\lambda b^*\rho^*$ is very nearly a straight line whose slope is -1, the same for all values of P and T, so that the entire P–ν–T surface of all nonpolar substances can be collapsed into single straight line by a suitable plot. In practice, only small deviations from accurate experimental results were found; a small adjustment was therefore applied to produce improved agreement.[4]

The present correlation procedure can be generalized to mixtures of any number of components; a formal extension of Eq. 1a to mixtures can be written as[7]

$$P/\rho RT = 1 + \rho \sum_{ij} x_i x_j (B_{ij} - \alpha_{ij}) F_{ij} + \rho \sum_{ij} x_i x_j \alpha_{ij} G_{ij}, \tag{4a}$$

where x_i and x_j are the mole fractions, $F_{ii}^{-1} = 1 + 0.22\lambda b^*\rho^*$ and $G_{ii}^{-1} = 1 - \lambda b^*\rho^*$. The simplest combining rules for predicting unlike-molecule interactions from the like-molecule interactions are a geometric mean for ΔH_v and an arithmetic mean for ρ_t. Thus, our combining rules would be

$$(\Delta H_\mathrm{v})_{ij} = [(\Delta H_\mathrm{v})_i (\Delta H_\mathrm{v})_j]^{\frac{1}{2}} \tag{4b}$$

and

$$(\rho_\mathrm{t})_{ij}^{-1/3} = 1/2[(\rho_i)^{-1/3} + (\rho_j)^{-1/3}]. \tag{4c}$$

Table 1. Volumetric Behavior of 0.5 Benzene +0.5 Hexane Liquid Mixtures

		Molar volume/$\mathrm{cm^3\ mol^{-1}}$		
T/K	P/bar	COSTALD[a]	Calcd	Dev/%
343.15	15.0	118.39	116.91	1.3
	20.0	118.25	116.84	1.2
	25.0	118.10	116.77	1.1
	30.0	117.96	116.70	1.1
	35.0	117.82	116.63	1.0
	40.0	117.68	116.56	0.96
	45.0	117.54	116.50	0.89
	50.0	117.40	116.43	0.83
	100.0	116.13	115.80	0.29
	150.0	114.98	115.21	−0.20
	200.0	113.94	114.66	−0.62
	250.0	112.99	114.14	−1.0
	300.0	112.11	113.65	−1.4
	400.0	110.53	112.76	−2.0
353.15	15.0	120.30	118.65	1.4
	20.0	120.14	118.57	1.3
	25.0	119.98	118.48	1.3
	30.0	119.82	118.40	1.2
	35.0	119.66	118.32	1.1
	40.0	119.51	118.24	1.1
	45.0	119.36	118.16	1.0
	50.0	119.21	118.09	0.95
	100.0	117.80	117.34	0.39
	150.0	116.55	116.65	−0.09
	200.0	115.42	116.02	−0.51
	250.0	114.40	115.42	−0.89
	300.0	113.45	114.87	−1.2
	400.0	111.77	113.85	−1.8
373.15	15.0	124.49	122.57	1.6
	20.0	124.29	122.45	1.5
	25.0	124.08	122.34	1.4
	30.0	123.88	122.22	1.4
	35.0	123.69	122.11	1.3
	40.0	123.49	122.00	1.2
	45.0	123.30	121.89	1.2
	50.0	123.12	121.78	1.1
	100.0	121.39	120.76	0.52
	150.0	119.89	119.83	0.05
	200.0	118.55	118.98	−0.36
	250.0	117.35	118.20	−0.72
	300.0	116.26	117.48	−1.0
	400.0	114.34	116.18	−1.6
393.15	15.0	129.30	127.17	1.7
	20.0	129.03	127.01	1.6
	25.0	128.77	126.85	1.5
	30.0	128.51	126.69	1.4
	35.0	128.26	126.53	1.4
	40.0	128.01	126.37	1.3
	45.0	127.77	126.22	1.2
	50.0	127.53	126.07	1.2
	100.0	125.37	124.66	0.57
	150.0	123.53	123.42	0.09
	200.0	121.93	122.29	−0.30
	250.0	120.51	121.28	−0.63
	300.0	119.24	120.35	−0.92
	400.0	117.04	118.71	−1.4

a) Corresponding States Liquid Density.[8)]

Table 2. Volumetric Behavior of Benzene+Octane Liquid Mixtures at 373.15 K and Six Compositions

		Molar volume/$\mathrm{cm^3\ mol^{-1}}$		
$x(\mathrm{C_6H_6})$	P/bar	COSTALD[a]	Calcd	Dev/%
0.0	15.0	179.15	181.20	−1.1
	20.0	178.93	181.10	−1.2
	25.0	178.71	181.00	−1.3
	30.0	178.50	180.91	−1.3
	35.0	178.28	180.81	−1.4
	40.0	178.07	180.72	−1.5
	45.0	177.86	180.63	−1.5
	50.0	177.66	180.53	−1.6
	100.0	175.72	179.65	−2.2
0.20	15.0	162.57	164.45	−1.1
	20.0	162.37	164.36	−1.2
	25.0	162.17	164.27	−1.3
	30.0	161.98	164.18	−1.3
	35.0	161.78	164.09	−1.4
	40.0	161.59	164.00	−1.5
	45.0	161.40	163.91	−1.5
	50.0	161.22	163.83	−1.6
	100.0	159.46	163.00	−2.2
0.40	15.0	146.20	147.74	−1.0
	20.0	146.03	147.66	−1.1
	25.0	145.85	147.57	−1.2
	30.0	145.68	147.49	−1.2
	35.0	145.51	147.41	−1.3
	40.0	145.34	147.32	−1.4
	45.0	145.17	147.24	−1.4
	50.0	145.01	147.16	−1.5
	100.0	143.45	146.39	−2.0
0.60	15.0	130.06	131.10	−0.79
	20.0	129.91	131.02	−0.85
	25.0	129.76	130.94	−0.90
	30.0	129.61	130.87	−0.96
	35.0	129.46	130.79	−1.0
	40.0	129.32	130.71	−1.1
	45.0	129.17	130.64	−1.1
	50.0	129.03	130.56	−1.2
	100.0	127.69	129.85	−1.7
0.80	15.0	114.16	114.57	−0.35
	20.0	114.03	114.49	−0.41
	25.0	113.90	114.42	−0.46
	30.0	113.78	114.35	−0.50
	35.0	113.66	114.28	−0.54
	40.0	113.54	114.21	−0.59
	45.0	113.42	114.14	−0.63
	50.0	113.30	114.07	−0.67
	100.0	112.18	113.41	−1.1
1.0	15.0	98.49	98.22	0.27
	20.0	98.39	98.15	0.24
	25.0	98.29	98.09	0.21
	30.0	98.19	98.02	0.17
	35.0	98.10	97.96	0.15
	40.0	98.00	97.89	0.11
	45.0	97.90	97.83	0.08
	50.0	97.81	97.76	0.05
	100.0	96.91	97.15	−0.24

a) Corresponding States Liquid Density.[8)]

Once $(\Delta H_\mathrm{v})_{ij}$ and $(\rho_\mathrm{t})_{ij}$ are known, the values of α_{ij}, b_{ij}, and B_{ij} follow from Eqs. 2a, 2b, and 2c as for pure substances. The quantities G_{ij} and F_{ij} for mixtures are given elsewhere.[7)] We had to test the combining rules given by Eqs. 4b and 4c, on compressed liquid mixtures. The results show that the density of liquid mixtures can be predicted within 5%. These are shown in Tables 1 and 2.

Results and Discussion

The previous statistical-mechanical theory would take ε and r_m based on the experimental values of $B_2(T)$, the second virial coefficient of the vapor.[2)] However, since $B_2(T)$, would not be known experimentally for many compressed liquids of interest, this method for finding suitable scale factor would be needed. The present work shows how the equation of state of a compressed liquid can be given a statistical-mechanical basis; this method is needed for applications to real molecular liquid mixtures. The P–ν from our two-parameter equation of state are given in Tables 1 and 2. The values were calculated from Eq. 4a using Eqs. 2a, 2b, and 2c in conjunctions with Eqs. 4b and 4c. The agreement is fairly good. We repeat that Eq.2 would be needed when the values of $B_2(T)$ are not experimentally known for most of the compressed liquids of interest.

The most important aspect of the present work is that the linear $\lambda b^* \rho^*$ dependence of the G^{-1} of any liquid can be given a strong basis in statistical mechanics. Moreover, the G can be calculated if ΔH_v and ρ_t are known. The present work also shows to what extent the results for compressed liquids can be extended, namely from critical up to the freezing density. This work shows useful (predictive) applications to real molecular liquid mixtures. The procedure has been tested on liquid mixtures ranging in complexity from benzene+n-hexane to benzene +n-octane.

In summary, although theory indicates that G is a function of a single variable $(b^* \rho^*)$ for pure substance, the fact that G^{-1} is nearly linear in $b^* \rho^*$ is empirical, and the numerical value of λ must be found from ρ_t. Furthermore, our equation of state appears to give accurate P–ν–T results at all liquid densities and temperatures. It is also simple in form and easy to use in a practical sense.

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