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Analytical Equation for Rigid Spheres: Application to the Model of Longuet-Higgins and Widom for the Melting of Argon

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Recent developments in the theory of fluids have produced an analytical expression for the *PVT* behavior of rigid-sphere fluids. The equation $(PV/NkT)^0=(1+y+y^2-y^3)/(1-y)^3$, where $y=b/4V=\sqrt{2}\pi N\sigma^3/6V$, has been shown to be the best analytical equation for rigid-sphere fluids presently known. Incorporation of the expression into the model of Longuet-Higgins and Widom for argon near its triple point, in a manner used by Guggenheim, demonstrates the sensitivity of predicted liquid behavior to the mathematical expression for rigid-sphere *PVT* behavior.

In 1964, Longuet-Higgins and Widom[1] proposed an equation of state for liquid and solid argon based upon a model of rigid spheres with attraction. Their equation is

$$p(n,T)=p^0(n,T)-an^2\,, \tag{1}$$

where $p^0(n,T)$ is the pressure which would be exerted by a system of rigid spheres at the same number density n and temperature T as the real system. The term $-an^2$ is a van der Waals-like uniform background cohesive pressure. The molecular dynamics calculations of Alder and Wainwright[2] were used for $p^0(n,T)$. However, in order to make certain integrations, they made use of the rigid-sphere equation of state resulting from "scaled particle theory" of Frisch[3,4] and his collaborators,

$$p^0(n,T)=nkT\,(1+y+y^2)/(1-y)^3\,, \tag{2}$$

where $y=b/4V=\sqrt{2}\pi V_0/6V$; $b=2\pi N\sigma^3/3$; σ is the rigid-sphere diameter; N is Avogadro's number; and $V_0=N\sigma^3/\sqrt{2}$ = molar volume at closest packing. In a subsequent paper, Guggenheim[5] carried out calculations for triple-point liquid properties, using only the Frisch equation (2) for rigid-sphere calculations. Guggenheim employed the Longuet-Higgins–Widom model for liquid argon successfully in this way. Calculated results agreed reasonably well with observed data. Agreement, however, was not perfect. In a later article, Guggenheim[6] repeated the calculations with several analytical rigid-sphere models. A tabular comparison of these results indicated that the calculated liquid properties are sensitive to the particular rigid-sphere equation employed.

In the present paper, the sensitivity of such calculations to the mathematical form of the rigid-sphere equation is investigated further. The predicted results are shown to improve when a more accurate expression for rigid-sphere behavior is used.

In 1969, a much-improved rigid-sphere equation[7] was developed from mathematical analysis of the reduced virial coefficients for rigid spheres. The equation is

$$p^0(n,T)=nkT(1+y+y^2-y^3)/(1-y)^3\,. \tag{3}$$

Table I shows the relative abilities of Eq. (2) and Eq. (3) in describing the fluid behavior of rigid spheres as calculated by the method of molecular dynamics.[2] Based upon these results and the detailed comparison by Guggenheim[6] involving all other currently popular rigid-sphere equations, Eq. (3) appears to be the best contemporary analytical expression for rigid-sphere fluids. It has been shown[7] to outperform the Padé (3, 3) approximant of Ree and Hoover. There certainly seems to be no important difference between the results predicted by Eq. (3) and the molecular dynamics calculations up through the observed "fluid-solid" transition density of the rigid-sphere system. This transition density corresponds approximately to $(V/V_0)=1.50$.

Recalculation of liquid argon properties using rigid-sphere behavior predicted by Eq. (3) and a van der Waals-like cohesion term reveals im-

TABLE I. Rigid-sphere compressibilities.[a]

V/V_0	Z^f	Z^c	Z^{aw}
1.50	13.18	12.43	12.5
1.60	10.80	10.16	10.17
1.70	9.01	8.56	8.59
2.00	6.03	5.83	5.89
10.00	1.36	1.36	1.36
∞	1.00	1.00	1.00

[a] V_0 is the rigid-sphere volume at closest packing; $Z=PV/NkT$; Z^f is calculated from Eq. (2); Z^c is calculated from Eq. (3); Z^{aw} is the molecular dynamics value reported by Alder and Wainwright (Ref. 2).

proved agreement between calculated and observed quantities. The calculations are made in the same manner as those made by Guggenheim.[5] The Guggenheim results are compared with the results of the present work in Table II.

One can see that the triple-point behavior is better described by the more accurate rigid-sphere equation. In the case of four of the exhibited quantities, there exists no essential difference between predicted and experimentally observed values. The logarithm of the liquid phase triple-point compressibility factor, $ln(P_tV_t/RT_t)_l$, is predicted exactly. The ratio of the normal boiling temperature to the triple point temperature T_b/T_t also is predicted exactly. Neither of these quantities was predicted exactly by Guggenheim[5] using Eq. (2). Exact prediction also occurs for the quantity (P_cV_t/RT_c) using the more accurate Eq. (3). This is the product of the critical-point compressibility factor (P_cV_c/RT_c) and the volume ratio (V_t/V_c). Because V_c is so difficult to measure, it is found that the prediction of (P_cV_t/RT_c) is more reliable. It is also found that an accurate prediction of the ratio of the Boyle temperature to the triple-point temperature T_B/T_t is possible with this model.

The remaining quantities in Table II are not as well-predicted as the above. This is attributable, in part, to the inability of this simple model to predict the critical point with accuracy. Guggenheim[5] discusses reasons for this in his paper. The calculated critical density is about $V_0/V_c = 0.18$ for Eqs. (2) and (3). Since both equations are essentially the same at low densities, the calculated value of the critical compressibility is the same for both equations, when rounded to two decimal places.

Thus, in summary, it has been demonstrated that an accurate analytical model of rigid-sphere PVT behavior exists. The values of rigid-sphere compressibility and the quasiexperimental data from molecular dynamics calculations show no strong differences up through very high densities. It has also been shown that Eq. (3) can be used effectively in the Longuet-Higgins–Widom model for the melting of argon. The results presented herein demonstrate that properties in the neighborhood of the triple point can be accurately described by an analytical rigid-sphere equation of state. An obvious advantage of having such an equation for the Longuet-Higgins and Widom model is that one is no longer dependent upon the tabular molecular dynamics values for accurately describing rigid-sphere behavior.

TABLE II. Triple-point calculations for argon.[a]

Property	Guggenheim[5]	Present work	Experiment
$(PV/NkT)_c$	0.36	0.36	0.29
T_t/T_c	0.535	0.540	0.557
y_c	0.129	0.131	0.161
T_B/T_t	5.02	4.92	4.91
P_cV_t/RT_c	0.109	0.108	0.108
$ln(P_tV_t/RT_t)_l$	−5.93	−5.89	−5.89
T_b/T_t	1.048	1.042	1.042

[a] c refers to the critical point; t refers to the triple point; l refers to the liquid phase; b refers to the normal boiling point; B refers to the Boyle temperature.

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