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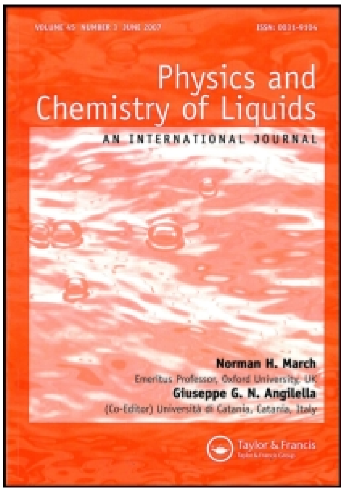

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Model Equations of State for Liquid Alkali Metals

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Letter

Model Equations of State for Liquid Alkali Metals

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The structure of a model equation of state for the liquid alkali metals is proposed, in response to the observed failure of the principle of corresponding states, and limited tests are presented.

Key Words: Model equation of state, liquid alkali metals.

The classical formula due to Van der Waals has formed the root of most attempts to describe simple liquid metals by model equations of state [1], and the increasing availability of high quality thermodynamic data on these systems permits a further examination of this subject.

Some years ago, Young and Alder[2] demonstrated that a simple Van der Waals equation of state, modified with the Carnahan-Starling hard sphere pressure, is of some relevance to the fluid alkali metals, although the predicted compressibility ratio, $Z_c = p_c V_c / R T_c$, is 0.36 compared with observed values between 0.06 and 0.21 through the series Li–Cs[3]. In recent work[3], we stressed the importance of long-range Coulomb interactions in these metals, and proposed a simple modification of the Young–Alder expression, incorporating a pressure term of the form $V^{-4/3}$ rather than the mean-field V^{-2} term. This was shown to lead to $Z_c = 0.146$, rather more in accord with the observed values. Indeed, we may note that Pfeifer *et al.*[4] obtained a corresponding term of the form $V^{-1.31}$ by regarding the exponent as a parameter to be fitted to experimental data on liquid rubidium. Nonetheless, as the variation of Z_c among the fluid alkalis indicates, 'corresponding states' does not apply, so that one is obliged to transcend these two-parameter equations of state.

As a starting point for the discussion below, we write the expression

$$[p_r + f_1(T_r, V_r)][V_r - \alpha] = \frac{T_r}{Z_c} f_2(T_r, V_r) \tag{1}$$

where $p_r = p/p_c$ etc. This form embraces many of the classical equations of state[5], so that, for example $f_1 = 3/V_r^2$, $\alpha = \frac{1}{3}$, $f_2 = 1$ generates Van der Waals, while $f_1 = 0$, $\alpha = \frac{1}{2}$, $f_2 = \exp(-2/V_r T_r)$ gives the Dieterici form.

We shall take f_1 to depend only on V_r, and form the thermal pressure coefficient $\gamma_V = (\partial p/\partial T)_V$ from Eq. (1). It is readily found that

$$\frac{1}{\gamma_V} = \left(\frac{V - \alpha V_c}{R}\right) g(T_r, V_r) \tag{2}$$

where

$$g(T_r, V_r) = \left[\frac{\partial}{\partial T_r}(T_r f_2)\right]^{-1}. \tag{3}$$

In particular, $g = 1$ for the original Van der Waals equation. In Figure 1 are plotted experimental data for $1/\gamma_V$ versus molar volume for points along the high density side of the liquid-vapour coexistence curve for the fluid alkali metals. The near linearity of each set of data over the range of temperature and density available provides good support for the form of Eq. (2), with $g(T_r, V_r)$ only a slowly varying function of its arguments. By extrapolation in the direction of low volume and temperature, it is found that $g \simeq 1.2$ here, in each case, while values of α lie in the range 0.12–0.16. It may be noted here that the modified Van der Waals expression referred to earlier, i.e.

$$p = \frac{RT}{V - b} - \frac{a}{V^{4/3}} \tag{4}$$

yields $\alpha = 0.14$ and $g = 1$. For direct experimental information regarding the critical region itself, one is, as yet, restricted to the heavy alkali metals. Hensel *et al.*[8] have produced a plot of the isochores of fluid caesium in this region, from which we find $\gamma_V V_c/R \simeq 1.2$. Estimating $\alpha = 0.14$, then, in Eq.(2) this leads back to $g(1,1) = 0.97$; close to the Van der Waals result. By way of contrast to Figure 1, the corresponding curve for the noble gas argon is given in Figure 2. Here, significantly greater curvature is observed, and the deviation from $g = 1$ is more substantial, even at low temperatures.

In summary, the form of Eq. (1) would appear useful, and some information on its components has been deduced from experimental data. A closer examination of Eqs. (1) and (2) requires more extensive and reliable thermodynamic data for the metals, particularly at high temperatures, and should prove illuminating, especially regarding the question of where the main source of deviation from corresponding states arises.

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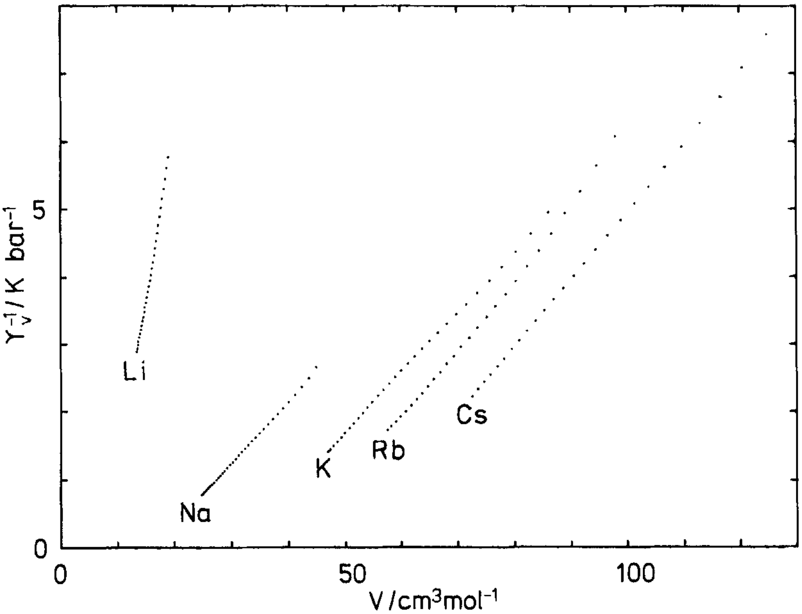

Figure 1 Inverse thermal pressure coefficient versus molar volume for the liquid alkali metals. Data from Ref. 6.

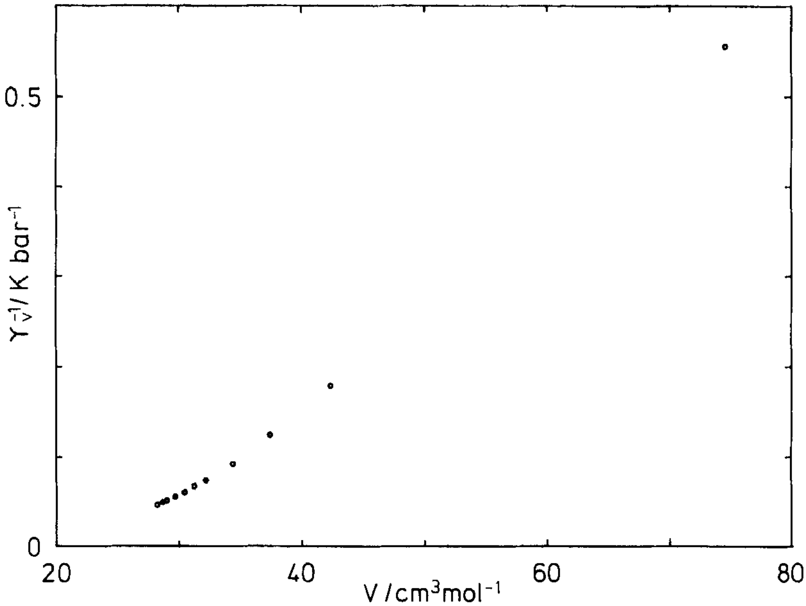

Figure 2 As in Figure 1, but for liquid argon. Data from Ref. 7.

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