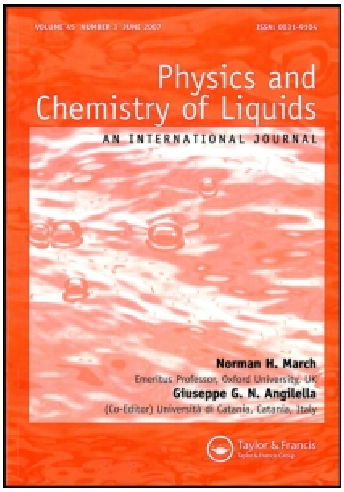

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QUANTITATIVE DESCRIPTION OF DEPARTURES FROM THE LAW OF RECTILINEAR DIAMETERS IN THE LIQUID–VAPOUR COEXISTENCE CURVES OF Rb AND Cs

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Using the experimental data of Hensel and co-workers for the liquid–vapour coexistence curve of Rb, it is demonstrated that the average density $(\rho_l + \rho_g)/2$, with l for liquid and g for gas, measured in units of the critical density, is linear in the variable $(1-(T/T_c))^{2/3}$, T_c being the critical temperature. The long-range polarization interaction exposed by Blazej and March in liquid metals is proposed as the underlying reason for this marked departure from the law of rectilinear diameters.

Keywords: Rectilinear diameters; Fluid metals

Much progress has come in understanding the behaviour of the low density fluid alkalis through the experiments of Hensel and his colleagues, both using neutron scattering to study structure and also by thermodynamic measurements. In this Letter, it is the latter that provide the focus, and especially the mapping experimentally of the liquid–vapour coexistence curves of Rb and Cs [1]. One of the

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*Corresponding author.

striking results of these measurements was the demonstration of marked departures from the law of rectilinear diameters, which has previously been discussed in Refs. [2–4]. Here, we shall take a strictly phenomenological approach, motivated by the early work of Guggenheim [5], who was however concerned with insulating fluids, such as neon and ethylene. Defining the difference density $\rho_l - \rho_g$, scaled with the critical density ρ_c, *i.e.*, the variable

$$\eta = \frac{\rho_l - \rho_g}{\rho_c} \tag{1}$$

where l denotes liquid and g gas, and the sum

$$\zeta = \frac{\rho_l + \rho_g}{2\rho_c} \tag{2}$$

which evidently means $\zeta = 1$ at the critical point, the assumptions of Guggenheim [5], as already noted by March, Tosi and Chapman [6], lead to the relation

$$\zeta = 1 + \frac{6}{343}\eta^3 \tag{3}$$

As pointed out in [6], this relation is a solution of the non-linear differential equation

$$\eta\frac{d^2\eta}{d\zeta^2} + 2\left(\frac{d\eta}{d\zeta}\right)^2 = 0 \tag{4}$$

Guggenheim's work [5] exhibiting a linear relation between η^3 and ζ for both Ne and ethylene, is not reproduced when the same plot is made for the metallic fluids Rb or Cs. This has led us to generalize Eq. (3): which is a direct consequence of Guggenheim's assumptions [5], to the form

$$\zeta = 1 + \varkappa\eta^\Gamma \tag{5}$$

Then it is easy to show that the differential equation becomes

$$\eta\frac{d^2\eta}{d\zeta^2} + (\Gamma - 1)\left(\frac{d\eta}{d\zeta}\right)^2 = 0, \tag{6}$$

being therefore a generalization of Eq. (4), which is already appropriate for insulators such as Ne and C_2H_4, when Γ is chosen to be 3.

However, while it might seem that the assumption of the differential equation (6) is more powerful than the form (5), in fact the general solution of Eq. (6) is readily vertified to be

$$\zeta = \varkappa_0 + \varkappa\eta^{\Gamma} \tag{7}$$

where $\varkappa_0$ and $\varkappa$ are the two arbitrary constants required in the general solution of the second order differential equation. It follows from their respective definitions that, as we approach the critical point, η goes to zero, while ζ approaches unity. These boundary conditions determine the value of $\varkappa_0$ to be equal to one, thus regaining the form of Eq. (5).

Figure 1 shows the plot we have made for the heavy alkali metal Rb using the experimental data of Ref. [1] for the case $\Gamma = 2$, and

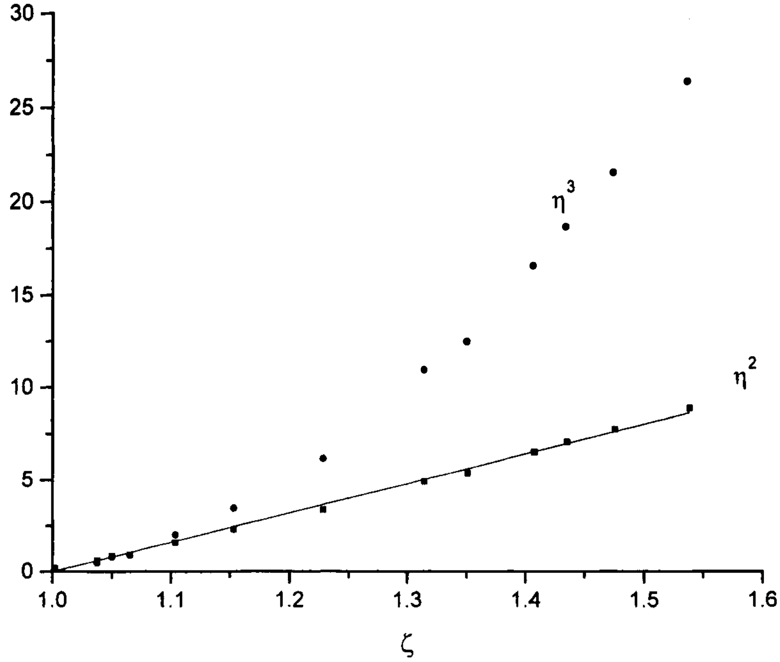

FIGURE 1 Shows experimental data of Jüngst *et al.* [1] along the liquid-vapour coexistence curve for Rb in the form of relations between difference density η defined in Eq. (1) and average density ζ in Eq. (2). It can be seen that the linear plot corresponds to η^2 *vs.* ζ. Guggenheim's form Eq. (3), valid for example for neon and ethylene, is plainly not appropriate for the metallic fluid Rb.

this is compared to the η^3 *vs.* ζ plot. The linearity of η^2 *vs.* ζ is striking, whereas plainly no such simple relation obtains for the η^3 plot. Thus our first conclusion is that Γ is markedly different as we go from the insulating fluids, where $\Gamma = 3$ works well as shown by Guggenheim [5], to the metallic fluid Rb, where $\Gamma = 2$ is the correct choice. Similar conclusions obtain for Cs though deviations in this fluid from the $\eta^2 - \zeta$ linearity are somewhat larger than for Rb.

However, if we examine Figures 2a and 2b, which plot η as a function of $(1 - (T/T_c))^{1/3}$ for Rb and Cs respectively from the experimental data of Jüngst *et al.* [1], their results are well represented by

$$\eta = \text{constant}\left(1 - \frac{T}{T_c}\right)^{1/3} \tag{8}$$

where 1/3 has been adopted as the ln–ln plots of Jüngst *et al.* [1] had slopes of 0.355 and 0.360 for Rb and Cs respectively. With $\Gamma = 2$ in Eq. (7) one is then led to the prediction

$$\zeta = 1 + \varkappa'\left(1 - \frac{T}{T_c}\right)^{2/3} \tag{9}$$

from the knowledge of η in Eq. (8).

Of course, the law of rectilinear diameters simply means that

$$\zeta = 1 + \text{constant}\left(1 - \frac{T}{T_c}\right) \tag{10}$$

and the marked departures for Rb and Cs are quantitatively described by the 2/3 rds power law in $(1 - (T/T_c))$ in Eq. (9), and not by the linear form Eq. (10) which is valid for example for Ne and C_2H_4 [5]. To press this point, experimental data [1] has been used to construct Figure 3 in which Eq. (9) is plotted directly. Finally, Figure 4 shows good agreement between the liquid–vapour coexistence curve for Rb, reconstructed from Eqs. (8) and (9), and the experimental data.

Naturally, it is important to discuss the fundamental origin of such different behaviour embodied in Eq. (9) for Rb and Cs from that for the insulating liquids. We propose here that it resides in the polarization term predicted by Blazej and March [7] in the effective pair potential $\Phi(r)$ between metallic ions in fluid alkali metals. This

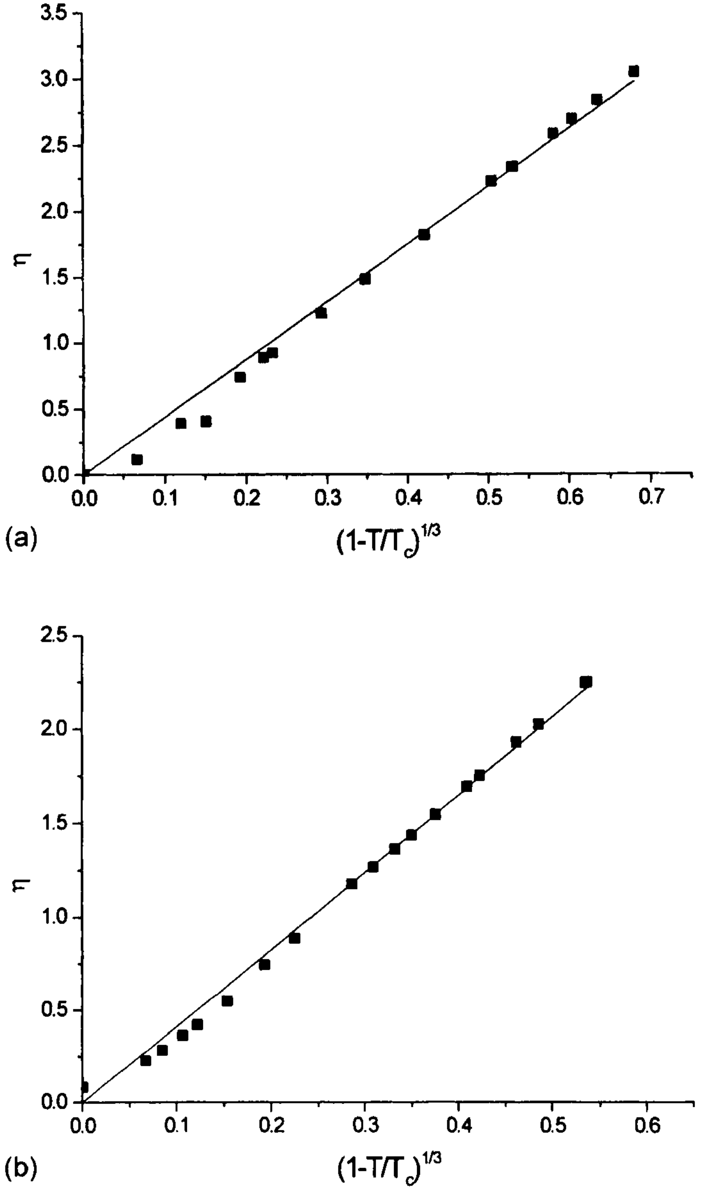

FIGURE 2 Difference density η plotted *vs.* $(1-(T/T_c))^{1/3}$, where T_c is the critical temperature, using the data of [1]. (a) metallic fluid Rb and (b) Cs. The slope of (a) has the value 4.36 ± 0.06 and for (b) its value is 4.12 ± 0.03.

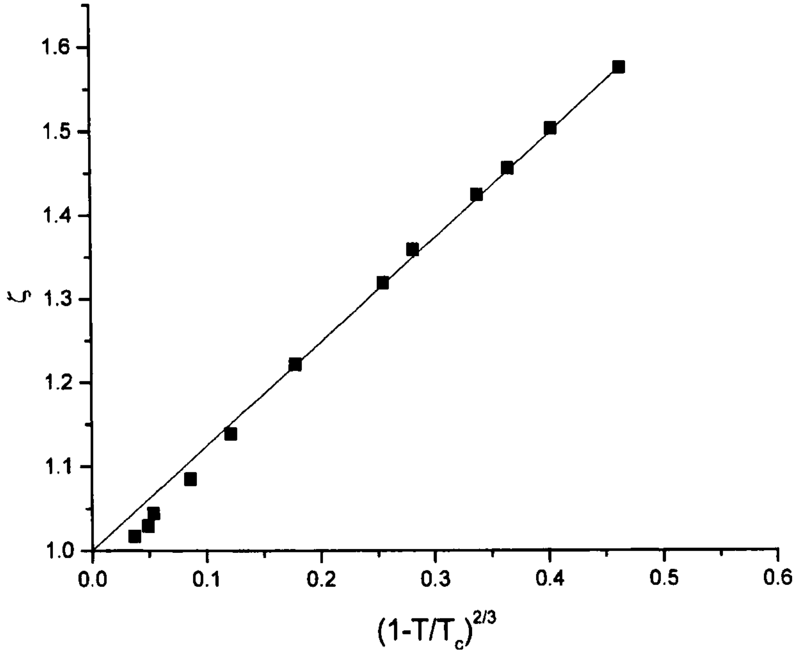

FIGURE 3 Average density ζ defined in Eq. (2) plotted for Rb *vs.* $(1-(T/T_c))^{2/3}$ from experimental data of Ref. [1]. Slope is 1.23 ± 0.03.

A similar plot for Cs shows larger deviations from linearity but a straight line through $\zeta=1$ at $T=T_c$ yields a somewhat similar slope of 1.02 ± 0.03.

leads to an attractive contribution to $\Phi(r)$ proportional to r^{-4} at sufficiently large ionic separation r. It might seem, at first sight that the pair interaction has an even longer range term of the form $(\cos(2k_f r)/r^3)$ ([8, 9]), where k_f is the Fermi wave number of the conduction electrons. However, since electrons have a finite mean free path, which from the Heisenberg Uncertainty Principle leads to blurring of the Fermi surface by an amount say Δk_f, a factor proportional to $e^{-\Delta k_f r}$ will eventually cause a 'damping' of the oscillatory term $(\cos(2k_f r)/r^3)$ at sufficiently large r and the polarization contribution proportional to r^{-4} will dominate. It is already stressed in Ref. [7] that if this polarization contribution to the effective pair potential is indeed present, a small angle neutron scattering experiment should lead to the fluid structure factor $S(k)$ having the small k form

$$S(k) = S(0) + a_1 k + a_2 k^2 + \cdots \tag{11}$$

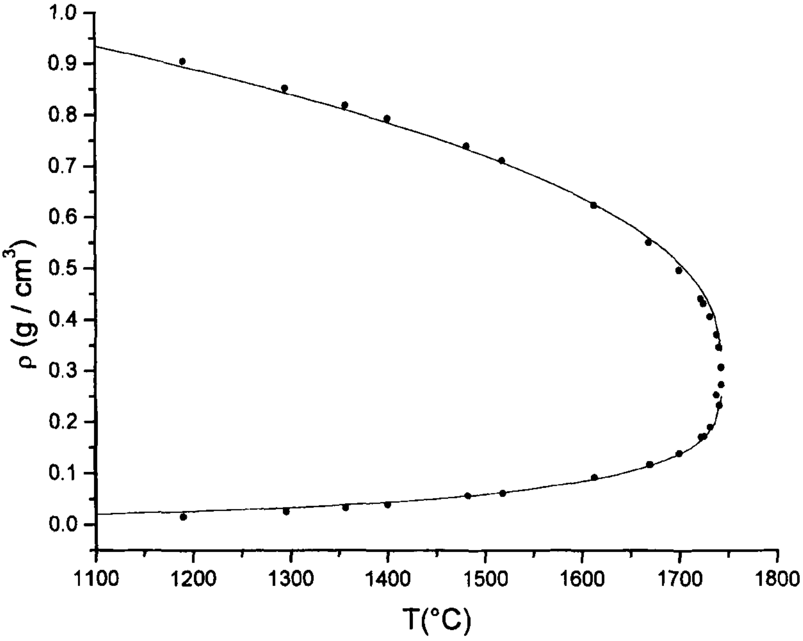

FIGURE 4 Shows quality of reconstruction of liquid-vapour coexistence curve for Rb. The circles represent the experimental data [1], whereas the continuous curves are obtained using the 1/3 and 2/3 power laws in Eqs. (8) and (9) for the difference density η and the average density ζ respectively, with the constants as recorded in the captions of Figures 2 and 3.

where

$$S(0) = \rho k_B T K_T \tag{12}$$

with ρ the number density and K_T the isothermal compressibility. a_1 is then directly related to the magnitude, c_4 say, of the pair potential asymptotic form $-c_4/r^4$ for the polarization contribution. It would clearly be of considerable interest within the present context if such a small angle scattering experiment could be carried out on low density metallic fluids such as Rb and Cs.

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