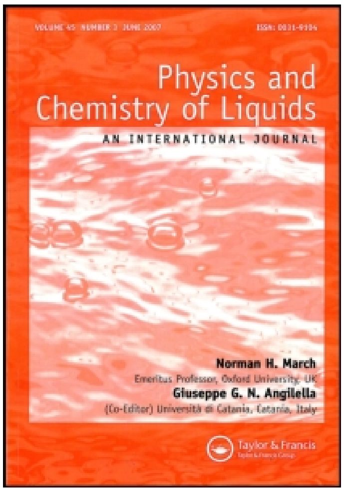

**Physics and Chemistry of Liquids**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

# Coordination-Dependent Equation of State of Expanded Liquid Alkali Metals and Critical Point Properties

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**To cite this Article** March, N. H. and Tosi, M. P.(1995) 'Coordination-Dependent Equation of State of Expanded Liquid Alkali Metals and Critical Point Properties', Physics and Chemistry of Liquids, 29: 3, 197 — 199
**To link to this Article: DOI:** 10.1080/00319109508028426
**URL:** http://dx.doi.org/10.1080/00319109508028426

*Phys. Chem. Liq.*, 1995, Vol. 29, pp. 197–199
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Gordon and Breach Science Publishers SA.
Printed in Malaysia

# LETTER

# Coordination-Dependent Equation of State of Expanded Liquid Alkali Metals and Critical Point Properties

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*(Received 17 October 1994)*

To take account of the known structure of expanded heavy alkali metals, a coordination number-dependent equation of state is set up. It is then shown that the critical constants $T_c$ and $V_c$ are related by $T_cV_c^{1/3} = \text{constant}$, while the compressibility ratio is no longer constant through the alkali series, as required by experiment.

Key words: Neutron scattering, plasma coupling parameter.

The neutron scattering experiments of Hensel and coworkers[1] on expanded liquid alkali metals Rb and Cs along the liquid-vapour coexistence curve have demonstrated that the liquid structure factors are characterized by (i) a remarkably constant near-neighbour distance and (ii) an almost linear decrease of coordination number c with decreasing liquid density.

The purpose of the present work is to propose a form for the equation of state which reflects the above variation of coordination number with the thermodynamic state. The proposal will then be confronted with experiments on the critical constants $p_c$, $V_c$ and $T_c$ of the alkali metal series ranging from Li to Cs.

Earlier theoretical work carried out independently by Chapman and March[2] and by Likalter[3] has expressed the pressure $p$ in the equation of state as the sum of two terms: namely an excluded volume contribution $p_{\text{ex}}$ and a Coulomb term $p_{\text{ch}}$ proportional to the plasma coupling parameter $\Gamma = (Z^2e^2n^{1/3})/k_BT$, where $Z$ is the valence and $n$ is the ionic density. The basic idea underlying the present treatment is to supplement these two terms by a third contribution to the pressure which is now coordination number-dependent. Thus we shall write for the pressure

$$p = p_{\text{ex}} + p_{\text{ch}} + p_{\text{coord}} \tag{1}$$

where $p_{\text{coord}}$ takes the form

$$p_{\text{coord}} = f(c, T). \tag{2}$$

The single further assumption will be made, before committing ourselves to quite specific models for the first two terms appearing in eqn (2), that

$$c = c(p, T) \tag{3}$$

which means, on combining Eqns. (1)–(3), that we are no longer dealing with an explicit form for the pressure $p$, but rather an implicit equation for $p$, due to the dependence of $p_{\text{coord}}$ on $p$.

We shall now follow Likalter[3] in modelling the excluded volume and Coulomb terms by writing

$$p = \frac{n(1+Z)k_BT}{1-nb} - \frac{1}{3}\alpha Z^2e^2n^{4/3} + f(c, T), \tag{4}$$

where $\alpha$ is the Madelung constant for the ionic assembly. Forming the spinodal curve defined by

$$\left(\frac{\partial p}{\partial n}\right)_T = 0 \tag{5}$$

we then obtain

$$p = \frac{1}{9}(1 - 4nb)\alpha Z^2e^2n^{4/3} + f(c, T). \tag{6}$$

The important point to note here is that since $p_{\text{coord}}$ does not depend explicitly on $n$, its pressure derivative does not enter the spinodal, since it will be multiplied by $(\partial p/\partial n)_T$ which is itself zero from Eqn. (5).

The critical point is located by imposing the condition $(\partial p/\partial n)_T = 0$ on the spinodal curve. One immediate and, to us, remarkable consequence of the proposed equation of state (1) is then that it yields

$$T_cV_c^{1/3} = \text{constant}. \tag{7}$$

This result is required from the empirical analysis of Chapman and March[2] who gave the exponent in Eqn. (7) as 0.3. That the value 1/3 followed from Likalter's work was pointed out very recently by Klein and March[4]. The specific results for the critical density and temperature are

$$n_c = \frac{1}{7b} \tag{8}$$

and

$$T_c n_c^{-1/3} = \frac{16\alpha Z^2 e^2}{49(1+Z)}. \tag{9}$$

In addition to Eqn. (7), there is a large variation in the compressibility ratio $Z_c$ defined by

$$Z_c = \frac{p_c V_c}{R T_c} \tag{10}$$

through the alkali series, ranging from 0.06 for Li to 0.20 for Rb and Cs. That such a situation is possible within the form of the equation of state proposed here becomes clear by forming $Z_c$ from Eqns. (6)–(9), the result being

$$Z_c = \frac{7}{48}(1+Z)\left[1 + \frac{21}{\alpha Z^2 e^2} n_c^{-4/3} f(c_c, T_c)\right]. \tag{11}$$

Evidently, without committing oneself to a form of the function $f$, the conclusion is simply that $Z_c$ does not follow as a constant through the alkali series.

While the result (7), in agreement with experiment already lends strong support to the assumptions (1)–(3), in work to be published elsewhere with D. J. Klein on crystalline metals, it can be shown that Eqn. (3) follows from current glue models of interatomic forces[5,6] at $T = 0$.

*Acknowledgements*

One of us (NHM) wishes to acknowledge the award of a Visiting Professorship at the Scuola Normale Superiore di Pisa in the latter part of 1994. His contribution to this work was brought to fruition during his stay in Pisa.

Support for this work is also acknowledged by NHM through the EC network on 'High energy density matter', coordinated by Professor J. M. Martinez-Val in Madrid. MPT acknowledges sponsorship and support from the Istituto Nazionale di Fisica della Materia.

Finally, a number of valuable discussions in this general area with Professor D. J. Klein are gratefully acknowledged.

*References*

1. See for example, R. Winter, W. C. Pilgrim and F. Hensel, *J. Phys.: Condens. Matter*, **6**, A245 (1994).
2. R. G. Chapman and N. H. March, *Phys. Chem. Liquids*, **16**, 77 (1986).
3. A. A. Likalter, *J. Phys.: Condens. Matter*, **4**, 10125 (1992).
4. D. J. Klein and N. H. March, *Phys. Chem. Liquids*, in press.
5. M. W. Finnis and J. E. Sinclair, *Phil. Mag.*, **A50**, 45 (1984).
6. I. J. Robertson, V. Heine and M. C. Payne, *Phys. Rev. Lett.*, **70**, 1944 (1993).