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S. M. Osman<sup>a</sup>; W. H. Young<sup>a</sup>

<sup>a</sup> School of Mathematics and Physics, University of East Anglia, Norwich, UK

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# A Model for Sub-critical Liquid–Vapour Coexistence in Sodium

S. M. OSMAN and W. H. YOUNG

*School of Mathematics and Physics, University of East Anglia,  
Norwich NR4 7TJ, UK*

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The Hamiltonian of the ions in liquid sodium is obtained from pseudopotential perturbation theory, and the free energy is evaluated using the Gibbs-Bogoliubov variational technique together with a hard sphere reference system. The free energy of the vapour is obtained by supposing it to be a monomer-dimer mixture. The two descriptions are then combined to provide a theory of coexistence. This yields satisfactory results for the various thermodynamic properties up to a few hundred degrees short of the critical temperature.

**KEY WORDS:** Monomers, dimers, hard spheres, pseudopotential.

## 1 INTRODUCTION

The problem of describing theoretically the liquid–vapour transition is more difficult for metals than for such simple non-metallic fluids as argon. This is because, in the case of metals, radical changes in the electronic states, from phase to phase, must be considered. Near the critical point, the character of the electronic states are not well-understood, but at lower temperatures and pressures, the situation is clearer and it is on this region that we focus.

The nearly free electron (NFE) theory of metals provides us with a description of ions, weakly coupled through the electron gas, but accompanied by a large volume-dependent but position-independent potential energy. On melting, the methods of classical liquid theory can be applied and, in the following, the Gibbs-Bogoliubov variational method, based on a hard sphere reference system,<sup>1</sup> is used.

Metallic vapours at low pressures are often regarded as monatomic and ideal but, in some cases, there is experimental evidence<sup>2</sup> that this view is not wholly correct. A macroscopic analysis<sup>3</sup> of the thermodynamic data for sodium, in particular, suggests dimerisation and we adopt this model below.

In the present work, we combine the above descriptions to obtain an account of the liquid-vapour transition in sodium. In an earlier paper<sup>4</sup> on this problem, the liquid was described essentially as indicated above but the vapour was taken to be an ideal monomer and a satisfactory account of coexistence was thus afforded up to about the 1 atm. boiling point (1156 K). With our improved picture, involving dimerisation, we can expect to obtain some success at higher temperatures and pressures and the degree to which this is achieved will be examined.

## 2 THE LIQUID

The theory here is widely known<sup>1</sup> so we provide below merely the basic formalism. Consider a liquid metal, of atomic mass  $M$ , valency  $z$ , and electron-ion pseudopotential  $v(q)$ , held at temperature  $T$  and specific volume  $\Omega_i$  (so that the free-electron Fermi wave index is  $k_F = (3\pi^2 z/\Omega_i)^{1/3}$ ). Then the Helmholtz free energy per atom can be written

$$F_l = F_{hs} + F_{eg} + F_1 + F_2 + F_M + \varepsilon_a \quad (1)$$

Here the first five contributions on the right of this equation, which we discuss shortly, give the free energy relative to a dispersed system of ion cores and valence electrons. The addition of  $\varepsilon_a$ , the valence electron binding energy per atom, creates a new zero of energy namely that of the monatomic vapour and this is a very convenient reference system when we come later to consider real (not necessarily monatomic) vapours.

Returning now to the first five contributions, we have

$$F_{hs} = -k_B T \{ \ln [e \Omega_i (M k_B T / 2\pi \hbar^2)^{3/2}] + S_\eta / k_B \} \quad (2)$$

$$F_{eg} = \left\{ \left( \frac{3}{10} \right) k_F^2 - \left( \frac{3}{4\pi} \right) k_F - 0.0474 \right. \\ \left. - 0.0155 \ln k_F - \frac{1}{2} (\pi k_B T / k_F)^2 \right\} z e^2 / a_0 \quad (3)$$

$$F_1 = \alpha / \Omega \quad (4)$$

$$F_2 = \frac{1}{2} (2\pi)^{-3} \int_0^\infty v^2(q) [\varepsilon^{-1}(q) - 1] S_{hs}(q) q^4 dq \quad (5)$$

$$F_M = - (6\sqrt{\pi} \eta)^{2/3} (1 - 0.2\eta + 0.1\eta^2) (1 + 2\eta)^{-1} z^2 / \Omega_i^{1/3} \quad (6)$$

and we comment briefly on each of these contributions.

$F_{hs}$ , given by Eq. (2), is the free energy of the hard sphere reference system. The first contribution is the ideal gas value and the second is the excess due to the finite size of the ions. As the notation implies, this is entropic and in the Percus-Yevick approximation<sup>5</sup> (compressibility route) used here, we have

$$S\eta/k_B = \ln(1 - \eta) - 3\eta(2 - \eta)/2(1 - \eta)^2 \quad (7)$$

Here  $\eta$  is the packing fraction, related to the effective hard sphere diameter  $\sigma$  by  $\eta = \pi\sigma^3/6\Omega_i$ . Equation (3) gives the electron gas free energy, the correlation energy being in Nozières-Pines approximation<sup>6</sup> and the final non-degeneracy term being of Sommerfeld form. Equation (4) corresponds to the expectation value with respect to the electron gas of the non-Coulombic portions of the pseudopotentials. Equation (5) arises from the indirect free-electron mediated interactions between the ions, the dielectric function  $\epsilon(q)$  being in Ichimaru-Utsumi form<sup>7</sup> and  $S_{hs}(q)$  being the analytically available<sup>5</sup> Percus-Yevick hard sphere reference structure factor. Finally, Eq. (6) corresponds to the direct, Coulombic, interactions between the ions, averaged over the associated Percus-Yevick hard sphere system.<sup>8</sup>

We next turn to the pseudopotential description. For  $v(q)$ , in (5), we take the empty core form<sup>9</sup>

$$v(q) = -(4\pi ze^2/q^2) \cos qr_c \quad (8)$$

where  $z$  is the valency ( $= 1$  for Na) and we can choose  $r_c$  numerically to give a satisfactory description of the entropy (see below). In simple conformity with (8), we might take, for use in Eq. (4),

$$\alpha = \lim[v(q) + 4\pi ze^2/q^2] = 2\pi ze^2 r_c^2$$

but it is known<sup>10,11</sup> to be necessary to improve upon this description for accurate results when volume is an important variable. This is certainly the case in the present study and we adopt here the empirical expression

$$F_1 = \frac{\alpha}{\Omega_i} = a\left(\frac{\Omega_b}{\Omega_i}\right) + b\left(\frac{\Omega_b}{\Omega_i}\right)^2 + c\left(\frac{\Omega_b}{\Omega_i}\right)^3 \quad (9)$$

Here  $\Omega_b$  is a reference specific volume and  $a$ ,  $b$  and  $c$  are constants with dimensions of energies. This form was used successfully by the present authors<sup>12</sup> in a preliminary study of Na and shown, a posteriori, to have a physical interpretation at least for this case. We will return to it again in Section 5.

Finally, for given  $T$  and  $\Omega_i$ , we choose the associated hard sphere diameter using the Gibbs-Bogoliubov condition

$$(\partial F_1/\partial \sigma)_{T, \Omega_i} = 0 \quad (10)$$

Once this condition is imposed, the entropy estimate becomes

$$S_l = -(\partial F_l / \partial T)_{\Omega_l} = S_{hs} + S_{eg} \quad (11)$$

where  $S_{hs} = (\frac{3}{2})k_B - F_{hs}/T$  and  $S_{eg} = (\pi k_B/k_F)^2 T z e^2/a_0$  arise from Eqs (2) and (3) respectively.

When the parametrisation is decided, we are in a position to calculate  $F_l(T, \Omega_l)$  and thence the other thermodynamic properties of interest. For example, the pressure is given by

$$P_l = -(\partial F_l / \partial \Omega_l)_T \quad (12)$$

and the Gibbs free energy by

$$G_l = F_l + P_l \Omega_l \quad (13)$$

### 3 THE VAPOUR

We next consider the vapour and suppose it to be a monomer-dimer mixture. The formalism is well documented, for example, by Landau and Lifshitz<sup>13</sup> and Rushbrooke<sup>14</sup> and we will merely summarise below the argument and main results.

Suppose there are  $N_1$  monomers and  $N_2$  dimers so that the total number of atoms, in single or combined forms, is  $N = N_1 + 2N_2$ ; it will be convenient below to speak, where necessary, of the  $N$  original atoms, to distinguish them from the  $N_1$  in monomeric form. We begin the analysis by noting that the Helmholtz free energy per original atom can be written as

$$F = F_1 + F_2 \quad (14)$$

where the  $F_i$  are calculated as though each species separately occupied the total volume  $V$ . The terms of this equation can be expressed in the form

$$F_i = -(N_i/N)k_B T \ln(eZ_i/N_i) \quad (15)$$

where the  $Z_i$  are discussed in more detail next.

For the monomer gas (of  $N_1$  atoms occupying the volume  $V$ ), we have

$$Z_1 = g(Mk_B T/2\pi\hbar^2)^{3/2} V \equiv \zeta_1 V \quad (16)$$

where  $g$  ( $=2$  in the case of Na) accounts for spin and orbital angular momentum degeneracy. Also, as in Section 2, we measure the energy relative to the electronic ground state. The alternative expression

involving  $\zeta_1$  has been introduced because it is useful later to isolate the volume dependence.

For the dimer gas contribution, we have

$$Z_2 = (2Mk_B T/2\pi\hbar^2)^{3/2} V \exp(\varepsilon_b/k_B T) Z_{\text{rotvib}} \equiv \zeta_2 V \quad (17)$$

where here, it will be noted, that the particle mass has been doubled, the spin degeneracy factor has been dropped,  $\varepsilon_b$  is the diatomic binding energy and a factor has been included to describe molecular rotation and vibration. The latter, in high temperature approximations, to be justified later, is written explicitly as

$$Z_{\text{rotvib}} = (T/2\theta_{\text{rot}})(T/\theta_{\text{vib}}) \quad (18)$$

Here

$$\theta_{\text{rot}} = \hbar^2/k_B MR^2, \quad \theta_{\text{vib}} = \hbar\omega/k_B \quad (19)$$

where,  $R$  is the bond length and  $\omega$  is the angular frequency of vibration. In Eq. (18), the division of the rotational factor by 2 occurs because the atoms within the molecule are identical.

From the above equations, other thermodynamic quantities may be calculated and, in particular, the pressure is

$$P = -(\partial F/\partial T)_V = \sum P_i; \quad P_i = N_i k_B T/V \quad (20)$$

and the Gibbs free energy per original atom is

$$G = F + PV/N = -\sum (N_i/N) k_B T \ln(Z_i/N_i) \quad (21)$$

We may use Eqs (20) and (21) to impose the condition for chemical equilibrium, which is  $(\partial G/\partial N_i)_{P,T}$  subject to the constraint that  $N_1 + 2N_2 = N$  remains constant. Thus, we obtain  $N_1 = \lambda Z_1$  and  $N_2 = \lambda Z_2$ , with  $\lambda$  chosen to conserve original atom number. On introducing  $\Omega_v \equiv V/N$ , the volume per original atom, we can write these results conveniently for our purpose as

$$N_1/N = \lambda \zeta_1 \Omega_v, \quad N_2/N = \lambda^2 \zeta_2 \Omega_v \quad (22)$$

and

$$(\lambda \zeta_1 + 2\lambda^2 \zeta_2) \Omega_v = 1 \quad (23)$$

In terms of the optimum  $\lambda$ , we find from Eqs (20) and (22) that the pressure at equilibrium is

$$P_v = (\lambda \zeta_1 + \lambda^2 \zeta_2) k_B T \quad (24)$$

while, from (21) and (22),

$$G_v = k_B T \ln \lambda \quad (25)$$

In the above formalism, electronic excitations have been neglected because, compared with the temperatures of interest, the energies involved are very high. For example, first ionisation potentials are of order several eV and  $1 \text{ eV} \equiv 1.2 \times 10^4 \text{ K}$ . Such temperatures are very much higher than the critical temperatures, at least for those metals (the alkalis, mercury) under active experimental investigation at present.

#### 4 LIQUID-VAPOUR COEXISTENCE

In Section 2 we considered a theory of the thermodynamic properties of a liquid metal and in Section 3 a theory for the corresponding vapour regarded as a monomer-dimer mixture. We must now consider the circumstances under which the two phases can coexist. The conditions for coexistence are that the pressures and Gibbs free energies of the phases are equal. Explicitly, for given  $T$ , we need to equate Eqs (12) and (24) to obtain

$$P_l(\Omega_l) = P_v(\Omega_v) \quad (26)$$

and Eqs (13) and (25) to obtain

$$G_l(\Omega_l) = G_v(\Omega_v) \quad (27)$$

Then these two equations must be solved for the unknowns  $\Omega_l$  and  $\Omega_v$ .

The solution of Eqs (26) and (27), for a specified  $T$ , can be conveniently obtained by the following search procedure:

- i) choose a numerical trial value for  $\Omega_l$
- ii) calculate  $P_l(\Omega_l)$  from Eq. (12)
- iii) calculate  $G_l(\Omega_l)$  from Eq. (13)
- iv) equate  $G_l(\Omega_l)$  and  $G_v(\Omega_v)$  and find  $\lambda$  from Eq. (25)
- v) use  $\lambda$  to find  $P_v(\Omega_v)$  from Eq. (24) and  $\Omega_v$  from Eq. (23)
- vi) compare the  $P_l(\Omega_l)$  and  $P_v(\Omega_v)$  found at stages (ii), (v)
- vii) revise  $\Omega_l$  at (i) until pressures agree at (vi).

This final  $\Omega_l$  at (vii) and the corresponding  $\Omega_v$  obtained at stage (v) are the required solutions for temperature  $T$ .

#### 5 PARAMETRISATION

So far, the description has been rather general, but now we focus on the special case of Na and consider its parametrisation. At low temperatures (in practice below about 1600 K), the liquid state properties are

**Table 1** Parameter input to calculations.

Symbol	Meaning	Value	Comment
$z$	Valency	1	
$r_c$	Pseudopotential core radius	0.91 Å	(a)
$a$	Characterise mean value of pseudopotential core	1.789 eV	
$b$		0.397 eV	(b)
$c$	(cf. Eq. (9))	0.187 eV	
$\epsilon_a$	3s atomic binding energy	5.344 eV	(c)
$\epsilon_b$	diatomic binding energy	0.7424 eV	(d)
$R$	diatomic bond length	3.079 Å	(d)
$\omega$	diatomic vibrational frequency	158 cm <sup>-1</sup>	(d)

(a) provides liquid state entropy fit over measured range (up to ~1400 K);

(b) provides liquid state Helmholtz free energy fit using Eq. (9) with a reference volume of  $\Omega_b = 51.49 \text{ \AA}^3$  (the measured 1 atm. boiling value);

(c) fitted to vapour pressure at 1200 K; differs slightly (see text) from measured value of 5.138 eV;

(d) measured spectroscopically by Kusch and Hessel.<sup>17</sup>

insensitive to vapour state considerations and thus this phase can be parametrised without reference to the other. For the vapour, the parameters can all be spectroscopically determined. Once the unknowns in each phase have been assigned, the main interest then lies in our ability to describe the higher temperature coexistence characteristics. We show, in Table 1 the parameters we use and, in the following subsections we elaborate on the reasons for these choices.

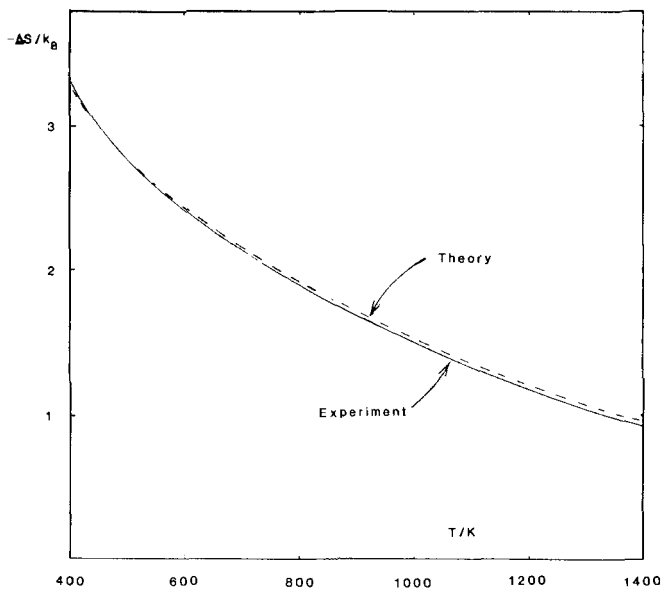
### (i) Liquid state

We need to specify the pseudopotential parameters appearing in Eqs (8) and (9). Addressing first Eq. (8), we take  $z = 1$ , for monovalency, and choose  $r_c = 0.91 \text{ \AA}$ , as this gives a good fit to the entropy over the measured range (Figure 1). Here, in making the fit, we have used the observed densities as input information. It will be noted that  $S_l$ , as given by Eq. (11) is independent of Eq. (4), so this exercise can be carried out without reference to the parametrisation of  $\alpha$  (see Eq. (9)).

Turning next to Eq. (9), we took the reference volume to be  $\Omega_b = 51.49 \text{ \AA}^3$ , which corresponds to the observed 1 atm. boiling point<sup>15</sup> and, after some trial and error, the values of  $a$ ,  $b$  and  $c$  shown in Table 1. This choice may be viewed† as a fit (again at the observed

† Any fit to the free energy must be done very accurately as we then require valid volume derivatives to obtain the pressure; we took care that this was so.





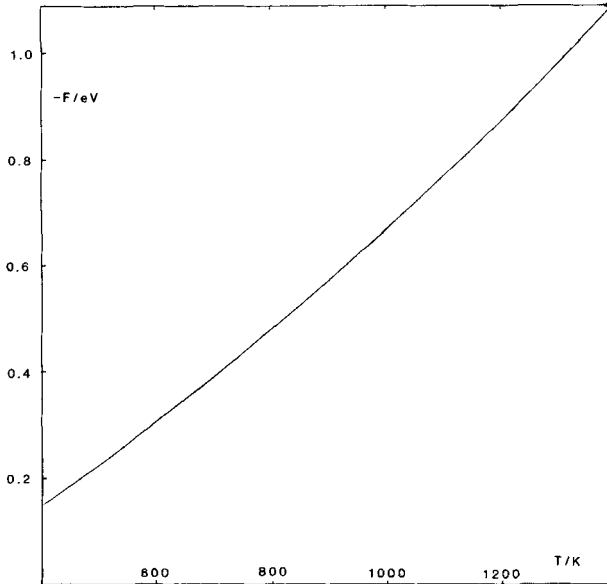
**Figure 1** Excess entropy  $\Delta S$  per atom of liquid Na over the observed range (vapour pressure negligible). The excess entropy is defined as the absolute value less that of a corresponding *structureless* gas occupying the same space; by the present theory, it is given by (cf. Eqs (2), (7) and (11))  $S\eta + S_{eg}$ . To obtain the excess entropy per atom relative to an ideal Na monomer vapour, add  $k_B \ln 2$  (cf. Eqs (15), (16)).

densities) over the measured range of the Helmholtz free energy; this is shown in Figure 2, where theory and experiment are identical to graphical accuracy. As expected (recall the remarks preceding Eq. (9)),  $\alpha$  is quite close numerically to  $2\pi z^2 e^2 r_c^2$ , but it is in fact its small departure from this value which is crucial for an accurate calculation of the pressure.

It is also convenient at this point to deal with the choice, in Eq. (1), of  $\varepsilon_a$  which, in the present context, represents the 3s valence electron binding energy. Experimentally, this is accurately known and given by 5.138 eV. However, we find it appropriate to change this value to 5.344 eV, thus obtaining the observed saturation vapour pressure at 1200 K. The essential point here is that this adjustment compensates for the small errors in the liquid state formalism (the first five terms of Eq. (1)) in calculating absolute free energies.

## (ii) Vapour state

The above mention of the ionisation potential  $\varepsilon_a$  for atomic sodium recalls our general statement at the end of Section 3 that electronic excitation and ionisation can be neglected. In the present case,  $T_c \approx$



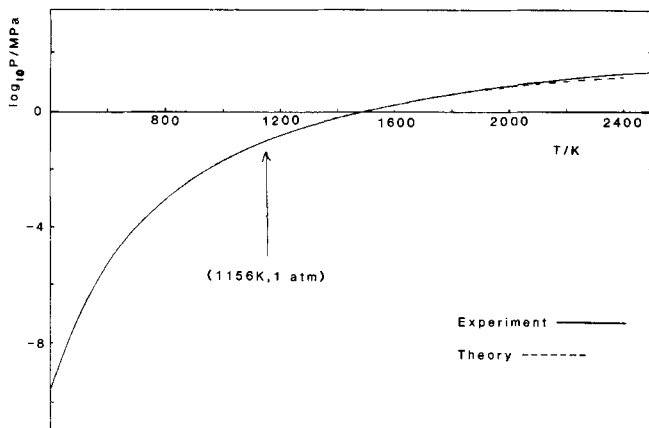
**Figure 2** Free energy per atom of liquid sodium over the observed range (in which, because of the low vapour pressure, the Helmholtz and Gibbs values essentially coincide). The theoretical and experimental results are indistinguishable to graphical accuracy when one makes the reasonable choice of 6.457 eV for the lattice energy per atom at absolute zero.

2500 K, so since  $\varepsilon_a = 5.138$  eV, we find  $\varepsilon_a/k_B T_c \approx 24$ , which is suitably high. In fact, our neglect of this effect is in agreement with the recent detailed study by Vargaftik and Voljak.<sup>16</sup>

The parameters appearing in Eqs (17)–(19) to characterise the sodium dimer are rather well-known from spectroscopic studies. We use here the data of Kusch and Hessel<sup>17</sup> and obtain  $\theta_{\text{rot}} = 0.2226$  K,  $\theta_{\text{vib}} = 228$  K and  $\varepsilon_b/k_B = 8616$  K, these figures corresponding respectively to a bond length of 3.079 Å, a vibrational frequency equivalent to 158  $\text{cm}^{-1}$  and a diatomic binding energy of 0.7424 eV. The parameters vary only a little from author to author and we have used them unchanged here. Because  $\theta_{\text{rot}}$  and  $\theta_{\text{vib}}$  are much smaller than the temperatures of interest in the present work, we are amply justified in using the high temperature forms shown in Eq. (19).

## 6 RESULTS

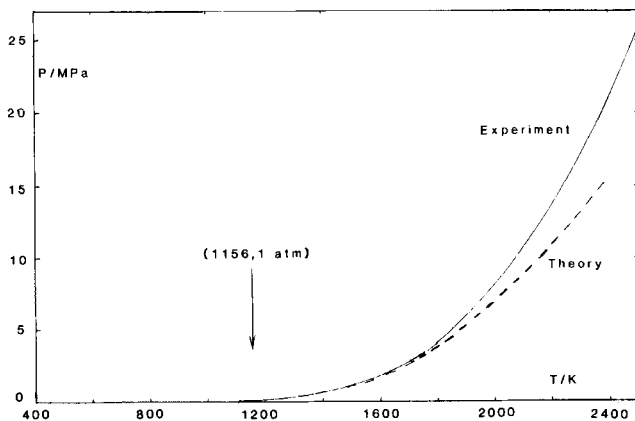
We show first, in Figures 3 and 4, the saturated vapour pressure calculated as a function of temperature. It is clear from Figure 3 that the experimental curve is well described, in order of magnitude, over the



**Figure 3** Saturated vapour pressure (logarithmic scale) versus temperature. The experimental curve shown is given by the formula of Browning and Potter,<sup>18</sup> which was fitted to the measured data.

whole range from 400 K to 2400 K and, in fact, the quantitative agreement is excellent, as Table 2 indicates, from the melting point up to well beyond the 1 atm. boiling temperature. However, as is seen clearly in Figure 4, a small discrepancy then sets in which becomes quite significant at the highest temperatures of interest.

Next, we indicate in Figure 5 the liquid–vapour density coexistence curve. It is clear from this diagram (see also Table 2) that the liquid density is given very accurately from the melting temperature up to very high temperatures; indeed above 2000 K the theory looks to be more



**Figure 4** Saturated vapour pressure versus temperature. As in Figure 3, except linear scale used for the pressure.

**Table 2** Liquid-vapour coexistence characteristics at two temperatures (near melting and near 1 atm. boiling).

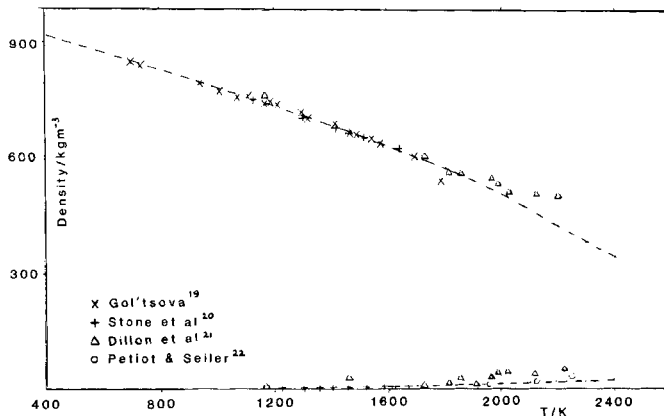
T/K	Saturated vapour pressure/MPa		Liquid density/kgm <sup>-3</sup>	
	Calc.	Expt.	Calc.	Expt.
400	$0.213 \times 10^{-9}$	$0.211 \times 10^{-9}$	911	920
1200	0.149	0.149	732	731

reliable than the experimental data. It is not so easy to assess the quality of the comparison between theory and experiment for the vapour on this graph, so we show some of the same data on an expanded scale in Figure 6. It is clear from this plot that, as for the pressure in Figure 4, a slight disparity sets in and develops as the temperature is raised above the 1 atm. boiling point.

A valuable method for obtaining insight into the above results is to plot the so-called compressibility factor  $P_v \Omega_v / k_B T$  against temperature and this is done in Figure 7. According to Eqs (22) and (24),

$$Z_c \equiv P_v \Omega_v / k_B T = (N_1/N) + (N_2/N) \quad (28)$$

and the theoretically computed component parts of this equation are also displayed. It is evident that below  $\sim 1230$  K, our theory produces too few particles (a particle for this purpose being either a monomer or a dimer) while above this temperature the opposite obtains.



**Figure 5** Density versus temperature of liquid and vapour Na at coexistence. The experimental data (indicated and referenced on the figure) were taken from the summary graph given by Ohse *et al.*<sup>23</sup>

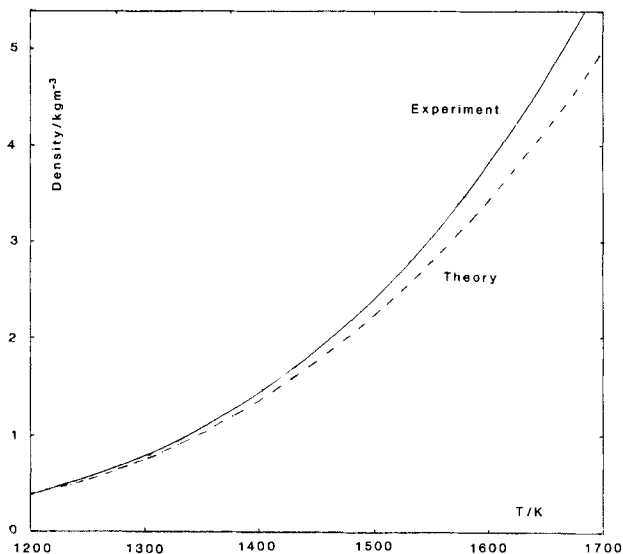


Figure 6 Density versus temperature of Na vapour at coexistence. Present theory is compared with the measured data of Stone *et al.*<sup>20</sup>

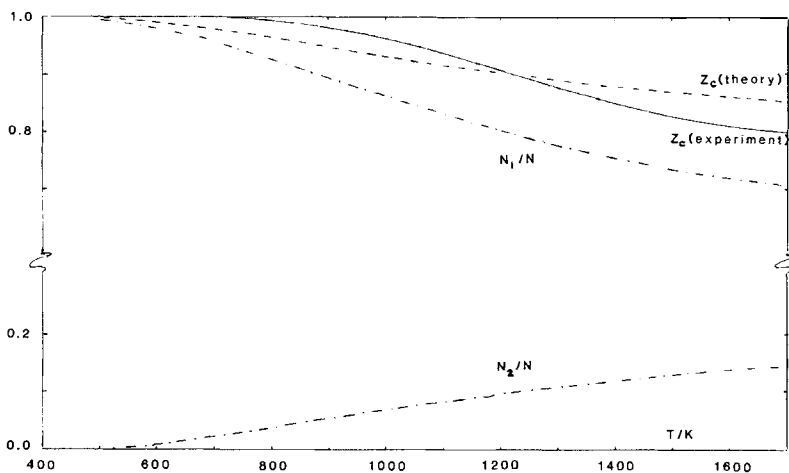


Figure 7 Vapour state compressibility factor  $Z_c \equiv P_v \Omega_v / k_B T$  versus temperature. Experimental results, from Hultgren *et al.*<sup>2</sup> are consistent with Figures 4 and 6. Theoretical results are also consistent with Figures 4 and 6. The monomer and dimer contributions,  $N_1/N$  and  $N_2/N$ , calculated according to Eq. (22) are also shown.

## 7 CONCLUSIONS

From the evidence of Figure 5, the NFE theory of the liquid appears to be valid up to about 2300 K. This is only some 200 K below the critical temperature and corresponds to about 1.8 times the critical density. Such a result is entirely in keeping with the experimental work by Franz *et al.*<sup>24</sup> on Rb. The effect of the finite (but small) vapour pressure is not easy to ascertain, since there are no observations in the region which matters most for forming a judgement. Nevertheless, our analysis in Ref. 12 suggests that some benefit has been obtained by allowing for this effect.

The gas theory is, at present, in less satisfactory form and this is most clearly revealed in Figure 7. Evidently the monomer-dimer model is an improvement on the ideal case but too few monomers result at lower temperatures and too many at higher temperatures. This has its effect on the pressure but the consequences only become serious as the highest temperatures are approached (Figures 4 and 6). Our theoretical results for the density in this region (Figure 6) produces an agreement with the measurements of Petiot and Seiler<sup>22</sup> but we would prefer to reserve judgement on the weight to be attached to this until a better description of the vapour is available to us.

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