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# Departures from Joule's Law in Dense Liquids near Freezing Related to Vacancy Properties in Hot Crystals

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The departures from Joule's Law that the internal energy  $U$  is independent of volume  $V$  are first expressed in dense liquids in terms of specific heats and the isothermal compressibility. For condensed rare gases, described by density independent pair potentials,  $(\partial U/\partial V)_T$  is shown to be closely related to the vacancy formation energy  $E_v$ , a correction term dependent on the density dependence of the pair function being displayed explicitly. For metals with density-dependent pair potentials,  $(\partial U/\partial V)_T$  is shown to involve the vacancy formation volume.

## 1 INTRODUCTION

In recent work, Bhatia and March<sup>1</sup> have shown that in condensed phases of rare gases, the approximate relation

$$[E_v + \frac{1}{2}B\Omega] = - \left( \frac{k_B T [c(r=0) + 2]}{2} \right)_{T_m} \quad (1.1)$$

holds,  $E_v$  being the vacancy formation energy,  $B^{-1}$  the isothermal compressibility  $K_T$ ,  $\Omega$  the atomic volume,  $c(r)$  the liquid direct correlation function and  $T_m$  the melting temperature.

However, it is known that  $E_v/k_B T_m$  is relatively constant for a wide variety of solids, and the present paper is concerned with understanding this particular correlation, which is evidently more specific than that embodied in Eq. (1.1).

What we shall find is that vacancy properties, both formation energy  $E_v$  and formation volume  $\Omega_f$ , can be usefully discussed in terms of departures from the so-called Joule's Law in dense liquids, which is stated as the independence of the internal energy  $U$  on volume. Specifically then, we shall focus on  $(\partial U/\partial V)_T$  in dense liquids. First of all, in Section 2 below,  $(\partial U/\partial V)_T$  will be approximately, but accurately, expressed in terms of specific heats  $c_p$  and  $c_v$  and compressibility  $K_T$ . It will be seen that this leads to the conclusion that  $[1/\rho k_B T (\partial U/\partial V)_T]$  evaluated near freezing is almost the same for liquid argon as it is for liquid metal rubidium,  $\rho$  being the liquid number density.

Then in Section 3, by invoking microscopic theory,  $(\partial U/\partial V)_T$  for liquid argon say, with density independent pair potentials, will be related to the vacancy formation energy  $E_v$  in the hot crystal. A 'correction term' will be exhibited which involves the density dependence of the liquid pair function  $g(r)$ . Metals are then contrasted with argon, and  $(\partial U/\partial V)_T$  will be shown to relate, though now not directly, to the vacancy formation volume  $\Omega_f$ .

## 2 DEPARTURES FROM JOULE'S LAW IN DENSE LIQUIDS

The usual thermodynamic formula relating the specific heat difference  $c_p - c_v$  to the coefficient of volume expansion and to  $K_T$  was earlier utilized by Bratby *et al.*<sup>2</sup> to obtain the following formula for the ratio of the specific heats  $\gamma = c_p/c_v$ :

$$\gamma = 1 + \frac{S(0)}{c_v} \left\{ \frac{p}{\rho k_B T} + \frac{1}{\rho k_B T} \left( \frac{\partial U}{\partial V} \right)_T \right\}^2 k_B. \quad (2.1)$$

Here the formula is written for a liquid state ( $p, \rho, T$ ), with  $S(0)$ , the long wavelength limit of the structure factor  $S(k)$ , related to  $K_T$  by the well known result of fluctuation theory

$$S(0) = \rho k_B T K_T. \quad (2.2)$$

The introduction of  $(\partial U/\partial V)_T$  into Eq. (2.1) was accomplished by utilizing the thermodynamic relation<sup>3</sup>

$$\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial p}{\partial T} \right)_V - p. \quad (2.3)$$

Below, we shall employ Eq. (2.1), together with experimental results for  $\gamma$ ,  $c_v$  and  $S(0)$ , to estimate the departures from Joule's Law in some dense liquids.

### 2.1 Estimates of $(\partial U/\partial V)_T$ in dense liquids

For dense liquids like argon near its triple point, one can now utilize Eq. (2.1) to estimate  $(\partial U/\partial V)_T$ .

The important simplification is to note that  $p/\rho k_B T \ll 1$ , and we therefore assume this term can be neglected in Eq. (2.2), to yield

$$\left| \frac{1}{\rho k_B T} \left( \frac{\partial U}{\partial V} \right)_T \right| \doteq \left\{ \frac{(\gamma - 1)(c_v/k_B)}{S(0)} \right\}^{1/2}. \quad (2.4)$$

Estimating Eq. (2.4) for argon near the triple point, where<sup>2</sup>  $\gamma \simeq 2.2$ ,  $c_v \simeq 2.3 k_B$ ,  $S(0) \simeq 0.06$ , one finds

$$\left| \frac{1}{\rho k_B T} \left( \frac{\partial U}{\partial V} \right)_T \right| \doteq 7, \quad (2.5)$$

confirming that this is indeed the dominant term in the bracket of Eq. (2.1).

For a liquid metal, say rubidium, near freezing,  $\gamma \simeq 1.23$ ,  $c_v \simeq 3.4 k_B$  while  $S(0) \simeq 0.023$  and hence from Eq. (2.4) we find Eq. (2.5)  $\sim 6$ .

In the following section, microscopic theory will be employed to relate such estimates of departures from Joule's Law in dense liquids to vacancy properties in hot close-packed crystals.

### 3 RELATION TO VACANCY PROPERTIES

To relate  $(\partial U/\partial V)$  to vacancy properties, Faber's formula<sup>4</sup> for the vacancy formation energy  $E_v$ , in the r-space formulation of Minchin *et al.*<sup>5</sup> will be invoked. This formula, restricted to close-packed solids because of its neglect of atomic relaxation round the vacant site, can be written in terms of the pair function  $g(r)$  and the pair potential  $\phi(r)$  as

$$E_v = \frac{-\rho}{2} \int g(r)\phi(r) dr \quad (3.1)$$

and following Bhatia and March<sup>1</sup> it can be usefully evaluated from the liquid pair function  $g(r)$  near freezing, to yield then the vacancy energy in the hot close-packed crystal.

What will be accomplished below is to relate  $E_v$  to  $(\partial U/\partial V)_T$ , utilizing microscopic liquid state theory. First we deal with the simplest case, exemplified by liquid argon, in which the pair potential  $\phi(r)$  is independent of the density  $\rho$ . Then, invoking the usual liquid state theory for the internal energy  $U$  one finds

$$\left( \frac{\partial U}{\partial V} \right)_T = -\frac{\rho^2}{2} \int \frac{\partial}{\partial \rho} [\rho g(r)] \phi(r) dr. \quad (3.2)$$

Utilizing the result (3.1) in Eq. (3.2) and dividing both sides by  $\rho k_B T$  yields

$$\left[ \frac{1}{\rho k_B T} \left( \frac{\partial U}{\partial V} \right)_T \right] = \frac{E_v}{k_B T} - \frac{\rho^2}{2k_B T} \int \frac{\partial g(r)}{\partial \rho} \phi(r) \, dr \quad (3.3)$$

For argon, we found in Section 2 that near the triple point the magnitude of the left-hand-side was  $\sim 7$ , whereas for condensed rare gas crystals at the melting point,<sup>1</sup>  $E_v/k_B T \simeq 9$ . Thus, within the present context it is clear that the dominant term in the vacancy formation energy of hot close-packed crystals is that arising from departures from Joule's Law, the 'correction term' in Eq. (3.3) involving the density dependence of the pair function contributing  $\sim 2$  to the equation at the melting point of argon.

### 3.1 Metals, with density-dependent pair potentials

For metals, one is dealing with density-dependent pair potentials  $\phi(r, \rho)$  and, in addition, one has a density-dependent structure independent term of electronic origin in the internal energy  $U$ , say  $U_0(\rho)$ .

We first outline an argument which, at least in principle, enables  $U_0(\rho)$  to be by-passed. Since the total pressure  $p \ll \rho k_B T$  under conditions we are presently discussing, we can write from Eq. (2.3) that

$$\frac{1}{\rho k_B T} \left( \frac{\partial U}{\partial V} \right)_T \simeq \frac{1}{\rho k_B} \left( \frac{\partial p}{\partial T} \right)_V \quad (3.4)$$

and since, for a pair potential model describing neutral pseudo-atoms we have again

$$p = \rho k_B T - \frac{\rho^2}{6} \int r \frac{\partial \phi}{\partial r} g(r) \, dr \quad (3.5)$$

$(\partial U/\partial V)_T$  can be evaluated from Eqs (3.4) and (3.5) as

$$\frac{1}{\rho k_B T} \left( \frac{\partial U}{\partial V} \right)_T \simeq \frac{1}{\rho k_B} \left[ \rho k_B - \frac{\rho^2}{6} \int r \frac{\partial \phi}{\partial r} \left( \frac{\partial g}{\partial T} \right)_V \, dr \right]. \quad (3.6)$$

Unfortunately,  $(\partial g/\partial T)_V$  is relatively inaccessible presently, and yet the term it enters is the dominant one in the form (3.6).

While the above argument allows  $U_0(\rho)$  to be avoided, in practice Eq. (3.6) does not presently appear to offer a practical way to proceed.

Therefore we return to the form of  $\partial U/\partial V$  for density-dependent potentials:

$$\begin{aligned} \left(\frac{\partial U}{\partial V}\right)_T &= \left(\frac{\partial U_0}{\partial V}\right)_T - \frac{\rho^2}{2} \int \frac{\partial}{\partial \rho} [\rho g(r)] \phi(r, \rho) \, \mathbf{dr} \\ &\quad - \frac{\rho^2}{2} \int \rho g(r) \frac{\partial \phi(r, \rho)}{\partial \rho} \, \mathbf{dr}. \end{aligned} \quad (3.7)$$

It is this form (3.7) that we now relate to vacancy properties, through the formula (3.1). Differentiating this with respect to density we find

$$\begin{aligned} \frac{\partial E_v}{\partial \rho} &= -\frac{1}{2} \int \frac{\partial}{\partial \rho} (\rho g(r)) \phi(r) \, \mathbf{dr} \\ &\quad - \frac{\rho}{2} \int g(r) \frac{\partial \phi(r, \rho)}{\partial \rho} \, \mathbf{dr} \end{aligned} \quad (3.8)$$

and hence combining Eqs (3.7) and (3.8) the result may be written

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U_0}{\partial V}\right)_T + \rho^2 \frac{\partial E_v}{\partial \rho} \quad (3.9)$$

We now utilize the thermodynamic formula<sup>6</sup> for the vacancy formation volume  $\Omega_f$ , namely

$$\Omega_f = \left(\frac{\partial E_v}{\partial p}\right)_T \quad (3.10)$$

to write

$$\Omega_f = \left(\frac{\partial E_v}{\partial \rho}\right)_T \left(\frac{\partial \rho}{\partial p}\right)_T. \quad (3.11)$$

But the isothermal bulk modulus is given by

$$B_T = -V \left(\frac{\partial p}{\partial V}\right)_T = \rho \left(\frac{\partial p}{\partial \rho}\right)_T \quad (3.12)$$

and hence, since  $K_T = B_T^{-1}$ ,

$$\Omega_f = \left(\frac{\partial E_v}{\partial \rho}\right)_T \cdot \rho K_T \quad (3.13)$$

or in terms of the atomic volume  $\Omega \equiv \rho^{-1}$

$$\frac{\Omega_f}{\Omega} = \rho^2 \left(\frac{\partial E_v}{\partial \rho}\right)_T K_T. \quad (3.14)$$

Hence it follows from Eq. (3.8) that

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U_0}{\partial V}\right)_T + \left(\frac{\Omega_f}{\Omega}\right) B_T \quad (3.15)$$

Finally one obtains from Eqs (3.15) and (2.5) that

$$\left\{\frac{(\gamma - 1)c_v/k_B}{S(0)}\right\}^{1/2} \doteq \frac{1}{\rho k_B T} \left(\frac{\partial U_0}{\partial V}\right)_T + \frac{\Omega_f}{\Omega} \frac{B_T}{\rho k_B T}. \quad (3.16)$$

This time, we are led to an expression in terms of specific heats and isothermal compressibility, a 'theory' concept,  $U_0(V)$ , together with the vacancy formation volume  $\Omega_f$ .

#### 4 SUMMARY AND DIRECTIONS FOR FURTHER WORK

It is fair to conclude that the major term in the ratio  $E_v/k_B T$  for argon crystal at the melting point can be associated with departures from Joule's Law in the liquid just above the melting temperature. It will clearly be of interest, for the future, to evaluate the 'correction term' in Eq (3.3) involving the density derivative of the pair function  $g(r)$ , either from computer simulation or from diffraction experiments.

The situation is less simple for metals, with density-dependent pair potentials. However, the approximate Eq. (3.16) relating observable properties such as specific heats and compressibility of the liquid metal just above its freezing point to vacancy formation volume may prove valuable as a check on theories of  $U_0(\rho)$ , the volume-dependent, structure independent contribution to the internal energy. This quantity still presents difficulties for theory and in this sense Eq. (3.16) seems also useful.

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