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AN EQUATION OF STATE IN THE CONDENSED PHASE FOR ARBITRARY PRESSURES  
AND MODERATE TEMPERATURES

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ABSTRACT

An equation of state for compressed matter is derived after assuming that its energy consists of vibrational energy which is a function of temperature only and of compressional energy which is a plausible function of volume only.



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AN EQUATION OF STATE IN THE CONDENSED PHASE FOR ARBITRARY  
PRESSURES AND MODERATE TEMPERATURES

We choose as independent parameters the volume  $v$  (of one mole) and the temperature  $T$ . Let  $u$  denote the internal energy,  $S$  the entropy, and  $p$  the pressure, the former two quantities again referred to one mole. Then

$$dS = \frac{pdv}{T} + \frac{du}{T} = \left( \frac{p}{T} + \frac{1}{T} \frac{\partial u}{\partial v} \right) dv + \frac{1}{T} \frac{\partial u}{\partial T} dT \quad (1)$$

From the equality of the two consequent second partials of  $S$ ,

$$\frac{\partial}{\partial T} \left( \frac{p}{T} + \frac{1}{T} \frac{\partial u}{\partial v} \right) = \frac{\partial}{\partial v} \left( \frac{1}{T} \frac{\partial u}{\partial T} \right)$$

we get:

$$\frac{\partial u}{\partial v} = T \frac{\partial p}{\partial T} - p \quad (2)$$

We make now the first assumption: The energy of the solid is representable as a sum of two functions of one variable each (the energy of compression depending on volume alone and the vibrational energy as a function of temperature only).

$$u = w(v) + c \cdot RT \quad (3)$$

(The constant  $c$  may be assumed  $= 3$ ; if one wants to take into account additional degrees of freedom,  $c$  may be modified accordingly.)



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From (2) the assumption (3) gives us

$$-w' = T \frac{\partial p}{\partial T} - p$$

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The integral of this differential equation for  $p$  gives us:

$$p = w' + Ta(v) \quad (4)$$

where  $a(v)$  is an arbitrary function to be determined by a further assumption. In fact, general thermodynamics can give us only a relation with one unknown function, even if one uses an assumption like (3).

One can get the form of  $a(v)$  by the following additional hypothesis: We assume that if the volume of the solid is changed, all vibrational frequencies in the lattice change by the same factor. We further assume that the vibrational frequencies do not depend on the temperature as long as the volume is constant. The latter assumption is satisfied only if the vibrations are harmonic (so these assumptions will not be justified at high temperatures).

We shall estimate the common factor by which all frequencies change by calculating the time sound takes to travel from an atom to its neighbor.

This gives the proportionality

$$\nu \approx s v^{1/3} \quad (\nu = \text{the frequency})$$

The sound velocity  $s$ , is given by:

$$s = \sqrt{\frac{\partial p}{\partial \rho}} = v \sqrt{-\frac{\partial p}{\partial v}}$$

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Using (4), we have

$$\psi = \psi_0 \sqrt{\frac{w}{w_0 + T a^2}}$$

In the approximation in which  $\psi$  is independent of  $T$  we can neglect in this expression the term  $T a^2(v)$ . In an adiabatic compression the number of quanta is unchanged. This means that the temperature-dependent part of  $u_0$ , namely  $\alpha RT_0$ , varies as  $\psi$ . For our adiabatic change we have therefore

$$T \sim \psi \sim v^{\frac{1}{3}} \sqrt{\frac{w}{w_0}} \quad (5)$$

The physical reason for the change of  $\psi$  is of course the change of volume during adiabatic compression. From (5) and from (1) we can get two expressions for  $\left(\frac{dT}{dv}\right)_S$  at constant entropy. Assuming therefore in (1) that  $dS=0$  we get

$$\left(\frac{dT}{dv}\right)_S = -\frac{p + (\partial u / \partial v)}{(\partial u / \partial T)} \quad (6)$$

Here  $p = w' + T a(v)$ ;  $\partial u / \partial v = -w'$ , and  $\partial u / \partial T = \alpha R$ . Thus

$$\left(\frac{dT}{dv}\right)_S = -T a / \alpha R$$

On the other hand from (5)

$$\left(\frac{dT}{dv}\right)_S \sim \frac{2}{3} \frac{1}{v} \sqrt{\frac{w}{w_0}} - \frac{1}{2} \frac{v^{\frac{1}{3}} w^{\frac{1}{2}}}{w}$$

This last proportionality has the same factor as in (5). We can write the equality

$$\left(\frac{dT}{dv}\right)_S = T \left( \frac{2}{3v} + \frac{1}{2} \frac{w'''}{w'} \right)$$



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Comparing this with the expression above we get:

$$\frac{-a}{\alpha R} = \frac{2}{3v} + \frac{1}{2} \frac{w'''}{w''} \quad (7)$$

This relation gives the function  $a(v)$  in terms of  $v$  and the function  $w(v)$ .

Our equation of state can be obtained if we take a plausible expression for the energy term  $w(v)$ . We shall use as an example the equation

$$w' = p_0 \left[ \left( \frac{v_0}{v} \right)^\gamma - 1 \right] \quad (8)$$

It should be noted that this approaches the elastic equation when  $v/v_0 \sim 1$ ,

and that  $w' \sim p^\gamma$  when  $v/v_0 \ll 1$ . From this equation we obtain

$$w'' = -p_0 \gamma \left( \frac{v_0}{v} \right)^{\gamma+1}$$

$$w''' = p_0 \gamma (\gamma + 1) \frac{v_0^\gamma}{v^{\gamma+2}}$$

Therefore

$$a(v) = -\alpha R \left( \frac{2}{3v} + \frac{1}{2} \frac{w'''}{w''} \right) = -\alpha R \left( \frac{2}{3v} - \frac{\gamma+1}{2v} \right)$$

$$a(v) = \frac{\alpha R (\gamma - 1)}{6v}$$

We now get as our equation of state

$$p = p_0 \left[ \left( \frac{v_0}{v} \right)^\gamma - 1 \right] + \frac{\alpha (\gamma - 1)}{6v} R T$$

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For the internal energy

$$u = -w(v) + \alpha RT$$

or

$$u = - \frac{P_0}{\gamma} \frac{v_0^\gamma}{v^{\gamma-1}} - P_0 v + \alpha RT$$

From (1) we get by integrating

$$S = \alpha R \left( -\frac{2}{3} \log v - \frac{1}{2} \log w^n + \log T \right)$$

or, since  $w^n = P_0^\gamma (v_0^\gamma / v^{\gamma+1})$ ,

$$S = \alpha R \left[ -\frac{2}{3} \log v - \frac{1}{2} \log \left( \frac{P_0^\gamma v_0^\gamma}{v^{\gamma+1}} \right) + \log T \right]$$

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