A thermodynamic model for pressurized solids

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Abstract. A thermodynamic model for solids under pressure is developed by assuming the universal equation of state and that under zero pressure the free energy is equal to the harmonic crystal (Debye) free energy. The model is applied to gold. In the case of nanocrystals this model reproduces the observed enhancement of the isobaric heat capacity and of the thermal expansion. Our model calculations are free of the ambiguities and inconsistencies connected with the Gruneisen equation, which was used in previous theoretical work.

1. Introduction

Recently, there has been great interest in nanocrystals, witness a recent review with 396 references [1]. These solids are of basic and technological interest since their properties are appreciably different from those of single crystals or those in polycrystalline samples. For example, the isobaric specific heat [2], C_p, and the thermal expansion coefficient [3], α, of metallic nanocrystals are enhanced and very rapidly with the excess volume of the solid occupied by the grain boundaries. The fact that the grain boundaries occupy a considerable portion of the volume of the nanocrystal leads to appreciably altered properties compared to 'macro' crystals.

Fecht's calculation [4], based on the universal equation of state (EOS) of Rose *et al* [5] and Slater's expression [6] for the Gruneisen parameter, γ, predicts that both C_p and α vary rapidly with excess volume. This calculation also predicts the unphysical result that the entropy diverges at a critical value of excess volume. Wagner [7], using the Debye–Gruneisen model and the Dugdale–MacDonald formula [8] for γ obtains enhancement of C_p and α without divergence of the entropy and the Gruneisen parameter.

In view of the uncertainty and arbitrariness involved in the definition of γ, we use in this paper a thermodynamically consistent model for heat capacity, thermal expansion, entropy, etc without making use of the Gruneisen parameter. The method is an application and extention of Smith's work [9], which concerns itself with the low-temperature quantum regime, to all temperatures. The model is based upon the finite-temperature Vinet *et al* universal EOS [5], which has been extensively tested on isothermal pressure–volume data for numerous metallic and covalent solids. Smith [9] integrated the universal EOS [5] to obtain an excess free energy. Our approach is to be contrasted to previous calculations, which started from the universal EOS but also involved further assumptions not necessarily consistent with the EOS. For example, Fecht [4] used both the universal EOS [5] and the Gruneisen EOS [10] and obtained a diverging entropy in violation of statistical mechanics. When our model is applied to metallic nanocrystals it yields the experimentally observed enhancement [2, 3] of the isobaric specific heat and thermal expansion, but no unphysical divergence of the entropy.

2. The thermodynamic model

The first step in our development is to obtain the fundamental thermodynamic equation, $F = F(V, T)$, from the universal EOS:

$$p = 3B_0[(1 - x)/x^2]\exp[\eta(1 - x)]$$ (1)

where F is the Helmholtz free energy, V is the volume, T is the temperature, p is the pressure, $x \equiv (V/V_0)^{1/3}$, B_0 is the zero-pressure isothermal bulk modulus, and $\eta \equiv 1.5[(\partial B/\partial p)_{p=0} - 1]$. Note that V_0, B_0, and η are functions of temperature only. Since $p \equiv -(\partial F/\partial V)_T$ one may obtain the free energy by integrating the equation of state [9]. Now assuming that at zero pressure $F(V, T)$ is equal to the free energy of the harmonic crystal (Debye model), F_D, we find

$$F(V, T) = F_D(T) - \int_{V_0}^{V} p \, dV.$$ (2)

(This implies that $C_p(T, p = 0)$ is equal to the harmonic Debye heat capacity at all temperatures; alternatively, one could use experimental values of the zero-pressure Gibbs potential for $F(V_0, T)$.) Substituting (1) and integrating yields the following fundamental equation:

$$F(V, T) = F_D(T) + 9V_0B_0\{1 + [\eta(1 - x) - 1]\exp[\eta(1 - x)]\}/\eta^2.$$ (3)

Note that, consistent with the EOS (1), the Debye free energy, F_D, must be a function of temperature only [11]. In (3) the volume dependence originates solely from the universal EOS. This differs from the Gruneisen approach where one assumes that the Debye temperature depends on volume. Next, the entropy is obtained from $S = -(\partial F/\partial T)_V$. Thus,

$$S(V, T) = S_D(T) - \left\{\frac{d}{dT}[9V_0B_0/\eta^2]\right\}\{1 + [\eta(1 - x) - 1]\exp[\eta(1 - x)]\}$$

$$- [9V_0B_0/\eta^2][\eta(1 - x)]\left[\frac{d\eta}{dT}(1 - x) + (\eta x\alpha_0/3)\right]\exp[\eta(1 - x)]$$ (4)

where α_0 is the zero-pressure thermal expansion coefficient and $S_D \equiv -dF_D/dT$. The heat capacity at constant volume is obtained from $C_V = T(\partial S/\partial T)_V$. Thus,

$$C_V = C_D - T\frac{d^2}{dT^2}[9V_0B_0/\eta^2]\{1 + [\eta(1 - x) - 1]\exp[\eta(1 - x)]\}$$

$$- 2T\frac{d}{dT}[9V_0B_0/\eta^2][\eta(1 - x)]\left[\frac{d\eta}{dT}(1 - x) + (\eta x\alpha_0/3)\right]$$

$$\times \exp[\eta(1 - x)] - T[9V_0B_0/\eta^2][\eta(1 - x) + 1]\left[\frac{d\eta}{dT}(1 - x) + (\eta x\alpha_0/3)\right]^2$$

$$\times \exp[\eta(1 - x)] - T[9V_0B_0/\eta^2][\eta(1 - x)]$$

$$\times \left[\frac{d^2\eta}{dT^2}(1 - x) + (2x\alpha_0/3)\frac{d\eta}{dT} + (\eta x/3)\frac{d\alpha_0}{dT} - \eta x\alpha_0^2/9\right]\exp[\eta(1 - x)].$$ (5)

The thermal expansion coefficient $\alpha \equiv (\partial \ln V / \partial T)_p$ and the isothermal bulk modulus $B_T \equiv -(\partial p / \partial \ln V)_T$ are obtained directly from the EOS (1):

$$\alpha = \alpha_0 - 3 \left[\frac{d \ln B_0}{dT}(1-x) + \frac{d\eta}{dT}(1-x)^2 \right] \bigg/ [2 + (\eta-1)x - \eta x^2] \qquad (6)$$

$$B_T = B_0[2 + (\eta-1)x - \eta x^2] \exp[\eta(1-x)]/x^2. \qquad (7)$$

Finally, the isobaric heat capacity, C_p, and the adiabatic bulk modulus, B_S, are obtained by substituting C_V, α, and B_T from (5), (6), and (7) into the thermodynamic identities

$$C_p = C_V + TV\alpha^2 B_T \qquad (8)$$

$$B_S = B_T[1 + TV\alpha^2 B_T / C_V]. \qquad (9)$$

We note that all the above formulae for thermodynamic quantities are valid at all temperatures, while the excess isochoric specific heat ΔC_v calculated by Smith [9] is only valid at very low temperature (in the quantum regime).

3. Application

We have applied this model to gold. The input data, which follow, are the temperature dependence of the equilibrium volume V_0 obtained from thermal expansion measurements [12] and polynomial fits of the equilibrium bulk modulus B_0 values [13] and of η values at temperatures between 300 K and 800 K.

$$V_0(T)/V_0(293) = 1 + 4.353 \times 10^{-5}(T-293) + 3.639 \times 10^{-9}(T-293)^2$$
$$+ 5.043 \times 10^{-12}(T-293)^3 \qquad (10)$$

$$B_0(T) = 180.83 - 0.0474T - 2.47 \times 10^{-6}T^2 \qquad (11)$$

$$\eta(T) = 8.604 + 7.111 \times 10^{-4}T + 3.664 \times 10^{-7}T^2 \qquad (12)$$

where B_0 is in gigapascals and T is in kelvin. The Debye temperature is 170 K [11].

The isothermal bulk modulus B_T versus $x = (V/V_0(T))^{1/3}$ at room temperature is shown in figure 1. Note that B_T vanishes at $x \approx 1.09$, signalling a thermodynamic instability. At the instability $\alpha = \infty$ and $C_p = \infty$. This follows from (6), (7), and (8), which imply that close to the instability $B_T \approx (x-x_I)$, $\alpha \approx (x-x_I)^{-1}$, and $C_p \approx (x-x_I)^{-1}$, where x_I is the value of the parameter x at the instability. The dependences of α and C_p on x at room temperature are shown in figures 2 and 3, respectively. The value of x_I is obtained by setting the right-hand side of (7) equal to zero:

$$x_I = +[\eta - 1 + \sqrt{\{(\eta-1)^2 + 8\eta\}}]/2\eta. \qquad (13)$$

The parameter η varies between about six and ten for metallic solids previously analysed by the universal EOS [5]. Hence, (13) yields values for the linear expansion parameter at the instability, x_I, in the range of 1.08–1.13. This range of values of x_I is comparable to Wagner's estimate for Pd ($x = 1.09$). Normally such an instability is associated with a phase transition. In the T, p plane the thermodynamic instability occurs at the line

$p = p_{\mathrm{I}}(T)$, which is shown in figure 4, and which was determined by using (1), (12), and (13). The proximity of this instability is responsible [4] for the observed enhancement of C_p in nanocrystals [2]. These materials have a lower density due to the non-negligible volume fraction of grain boundaries, i.e. $x = (V/V_0)^{1/3} > 1$. In figure 5 we show the temperature dependence of C_p for $x = 1$ (macrocrystal) and for $x = 1.075$ (nanocrystal). The enhancement in C_p is about 40%, not unlike the experimental [2] C_p for Pd. Finally, in figure 6, we plot the excess entropy, $\Delta S \equiv S - S_{\mathrm{D}}$, as given in (4) as a function of x at room temperature. There is no unphysical divergence of ΔS at the thermodynamic instability, unlike Fecht's prediction [4], and consistent with Wagner's [7] calculation. We note that the main approximation in this analysis is that the free energy of a nanocrystal is the same function of V and T as that of a macrocrystal.
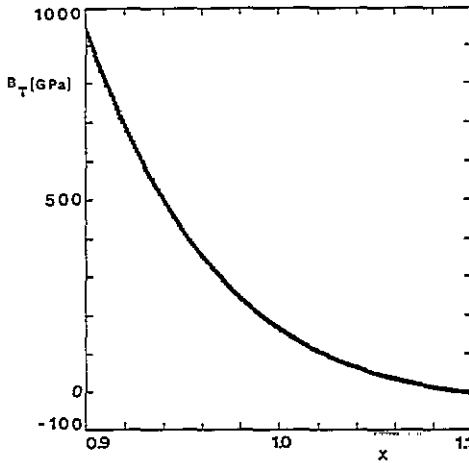

Figure 1. The isothermal bulk modulus, B_T, against $x = (V/V_0)^{1/3}$; $T = 300$ K.
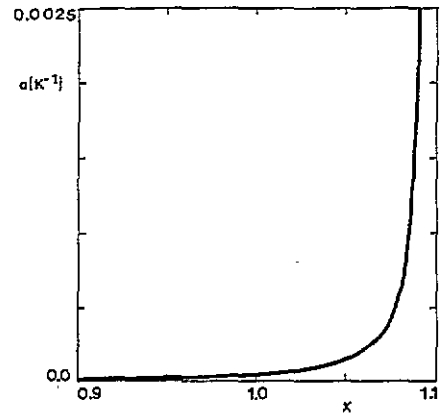

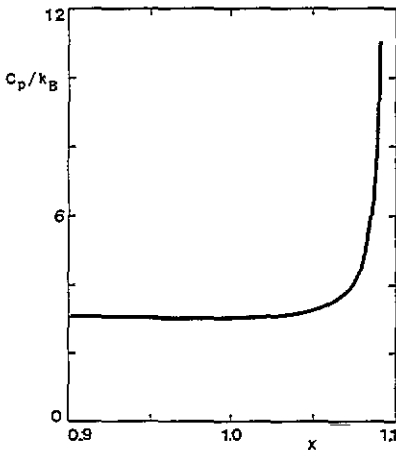**Figure 2.** The volume expansion coefficient, α, against $x = (V/V_0)^{1/3}$; $T = 300$ K.

Figure 3. The isobaric heat capacity, C_p (in units of k_{B}), against $x = (V/V_0)^{1/3}$; $T = 300$ K.
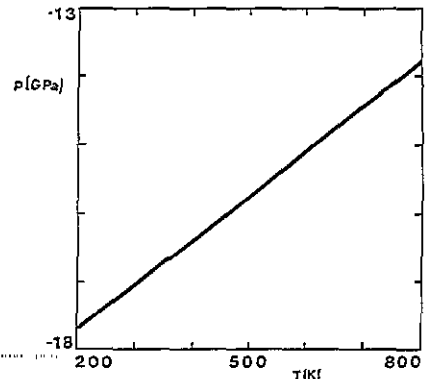

Figure 4. The instability line on the T, p plane; the solid is stable above the line.
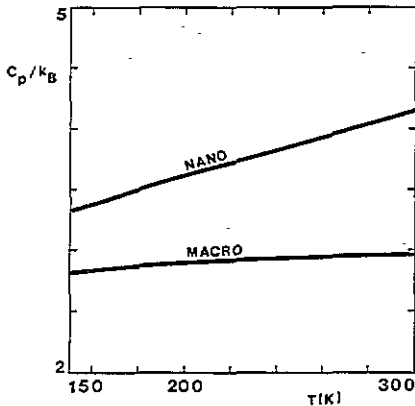
Figure 5. The isobaric heat capacity, C_p (in units of k_B), against T for $x = 1$ (macrocrystal) and $x = 1.075$ (nanocrystal).
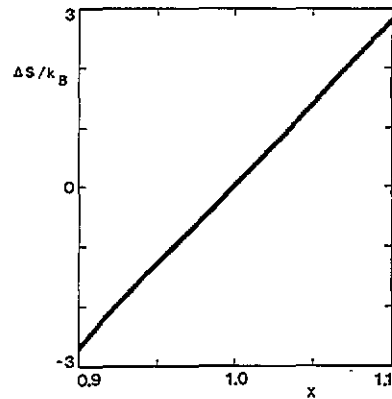
Figure 6. The excess entropy, $\Delta S = S - S_D$ (in units of k_B), against $x = (V/V_0)^{1/3}$; $T = 300$ K.

4. Conclusion

In conclusion, we have shown how to calculate the specific heats, the thermal expansion coefficient, the entropy, etc in a thermodynamically consistent way directly from the finite-temperature universal equation of state without use of the Gruneisen equation. We have found that the enhancements of C_p and α for metallic nanocrystals are in good agreement with experiment. The entropy remains finite, in agreement with expectations based on general statistical mechanics. Direct evidence supporting the concept of lower effective density due to grain boundaries in nanocrystals is provided by recent experimental studies [14] of nanocrystalline CdSe. It was observed that the transition pressure between the wurtzite and rock salt structures increases with decreasing grain size.

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