



# Coherent thermodynamic model for solid, liquid and gas phases of elements and simple compounds in wide ranges of pressure and temperature

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## ABSTRACT

Thermodynamic modeling of fluids (liquids and gases) uses mostly series expansions which diverge at low temperatures and do not fit to the behavior of metastable quenched fluids (amorphous, glass like solids). These divergences are removed in the present approach by the use of reasonable forms for the “cold” potential energy and for the thermal pressure of the fluid system. Both terms are related to the potential energy and to the thermal pressure of the crystalline phase in a coherent way, which leads to simpler and non diverging series expansions for the thermal pressure and thermal energy of the fluid system. Data for solid and fluid argon are used to illustrate the potential of the present approach.

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## 1. Introduction

A good representation of thermodynamic data for fluids (liquids and gases) started with the famous van der Waals equation [1], which contains one temperature independent term for the attractive potential energy and a second term for the temperature dependent kinetic energy of an ideal gas in a restricted space. In terms of pressure there is a temperature independent (cold) attractive pressure and a repulsive thermal pressure. More recent thermodynamic models use however most commonly virial type series expansions [2], some times with exponential damping factors, and a large number of adjustable coefficients (up to 84 in IAPS-84 [3]) or even different sets of 15 coefficients to represent the equation of state (EOS) for lower and higher ranges in pressure and temperature [4]. These large numbers of coefficients are needed, because these forms do not model correctly the potential energy and cold pressure with the effect that they diverge outside the range of the fitted data, most seriously at low temperatures, but also at high densities. Although one of the series expansions [5] includes a term for the “cold” pressure, the other terms add divergences at low temperatures, which require again a large number

of coefficients for accurate modeling.

Since one expects that metastable amorphous glassy states of quenched fluids at low temperatures as well as the states of fluids under very strong compression close to the melting line show similarities to the neighboring crystalline solid phases I propose to start also for the fluid phase from a potential energy (and cold pressure), with some correlations to the static lattice energy of the solid and add a non diverging series expansion only for the remaining thermal pressure of the fluid. This approach follows closely the thermodynamic modeling of solids, where the EOS for “regular” solids are very well understood even for extremely wide ranges in pressure [6–8].

## 2. The model

Since I would like to present a coherent picture for the modeling of the solid and fluid phases of “simple” crystalline materials (with no phase transitions in the range of interest) I may recall that EOS of these simple solids are very well represented over extremely wide ranges in pressure by an “adapted polynomial expansion” (APL), which interpolates between lower pressures and the well understood Fermi-gas behavior at extremely high pressures. In second order we have [6–8].

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$$pAP2(x) = 3 \cdot K_0 \cdot \frac{1-x}{x^5} \cdot e^{c_0 \cdot (1-x)} \cdot (1 + c_2 \cdot x \cdot (1-x))$$

with  $x = \sqrt[3]{V/V_0}$  for the linear compression.  $K_0$  represents the bulk modulus at ambient pressure for the given temperature.  $c_0 = \ln(aFG) - \ln(3 \cdot K_0) + \frac{5}{3} \cdot \ln\left(\frac{Z}{V_0}\right)$  depends on the total electron density  $Z/V_0$  at ambient pressure, the parameter  $aFG = 0.02337 \text{ GPa nm}^5$  takes care of the correct limiting behavior at very strong compression,  $c_2$  cares for the pressure derivative of the bulk modulus  $K_{so}$  (at ambient pressure):  $c_2 = \frac{3}{2} \cdot (K_{so} - 3) - c_0$ . Thereby the dependence of  $c_2$  on  $c_0$  provides very small values of  $c_2$  for “ideal solids” [6]. For the elements,  $Z$  is just the atomic number and  $V_0$  the atomic volume. When  $V_0$  refers to the specific volume and  $Z$  to the total number of electrons per Mole, one needs in addition the molar mass  $M$  to apply the AP2 form with a total of 5 parameters:  $Z$ ,  $M$ ,  $V_0$ ,  $K_0$ ,  $K_{so}$ .

The dominant contribution to the thermal pressure of crystalline solids is very well represented by the Grüneisen-Debye approximation [9–11]:

$$pSth(V, T) = \frac{\gamma(V)}{V} \cdot USth(V, T)$$

The Grüneisen parameter  $\gamma(V) = -\delta \ln(TD(V))/\delta \ln(V)$  decreases smoothly under pressure and represents the volume dependence of the Debye temperature  $TD(V)$  in the Grüneisen approximation for the thermal energy  $USth(T/D(V))$ . From the many different forms for the volume dependence of the Grüneisen parameter [12] I use here the form [13]:

$$\gamma(V) = \gamma_\infty + (\gamma_0 - \gamma_\infty) \cdot \left(\frac{V}{V_0}\right)^{\frac{\gamma_0 - \gamma_\infty}{\gamma_0 - \gamma_\infty}}$$

Higher order contributions for phonon dispersion, anharmonicity and defects lead to deviations from the Grüneisen model at higher temperatures, and are well understood [11], but are not needed here. The classical Grüneisen approximation does not include the quantum corrections, which dominate at temperatures below  $TD(V)$  and enter into the present form for the internal energy  $USth(T, V)$ .

For the modeling of the fluid phase I assume now that the potential energy or the isotherm for compression of the cold, amorphous, or glassy fluid must show some resemblance to the behavior of the crystalline solid. The disorder in the amorphous solid is expected to “smeared out” the potential energy in such a way that the potential minimum becomes broader and weaker than in the corresponding crystalline state. This means that the initial volume for the quenched fluid or amorphous solid should be larger than for the crystalline solid:  $V_{Fo} > V_{So}$ . For the bulk modulus we expect  $K_{Fo} < K_{So}$ , and values for parameters  $c_{Fo}$  and  $c_{F2}$  have to be adjusted correspondingly.  $F$  denotes thereby parameters for the fluid state and  $S$  for the crystalline solid also with respect to the previously given form for  $c_0$  and  $c_2$ . Since the APL-form was designed for solids under strong compression, it does not reproduce the region of negative pressures or large expansion perfectly. Its exponential “screening” factor falls off more rapidly than the dispersion forces typical for “simple” atomic fluids. These considerations lead to the use of a Mie-Grüneisen form [14] for the attractive part in the potential energy of the fluid phase and to the corresponding form for the pressure:

$$pMie(V) = \frac{K_0}{K_{so} - 4} \cdot \left(\frac{V}{V_0}\right)^{2-K_{so}} \cdot \left(1 - \left(\frac{V}{V_0}\right)^{K_{so}-4}\right)$$

whereby a smooth switching at  $V=V_0$  from  $pMie$  to  $pAP2$  is provided

by the use of the same parameters  $V_0$ ,  $K_0$ , and  $K_{so}$  for both forms. This means that the resulting forms for the cold pressure of the crystalline solid  $pSC(V, V_{So}, K_{So}, K_{SSo})$  and for the (extrapolated) cold pressure of the amorphous states  $pFC(V, V_{Fo}, K_{Fo}, K_{FSo})$  have the same analytical form and differ only in the parameters for the zero pressure values of the volume, bulk modulus, and its pressure derivative with the same values for the electron number  $Z$  and the molar mass  $M$ . This means that we have only 3 additional parameters for the EOS of the cold fluid.

The theoretical modeling of the thermal pressure for fluids is quite intriguing. Contributions from vibrational, librational, translational motion as well as from vacancies and cluster formation can not be separated easily. Therefore one needs a reasonable series expansion, which fits asymptotically to the ideal gas behavior at low densities and approaches a solid like behavior under strong compression. These considerations lead at first to the following form for the thermal pressure of the fluid:

$$pFth(V, T) = \frac{R \cdot T}{V} \cdot \left[1 + \sum_n a_n \cdot n \cdot B_n(T) \cdot \left(\frac{V_c}{V}\right)^n\right]$$

with temperature dependence in the functions

$$B_n(T, Bn1, Bn2) = (1 + Bn1 + Bn2) / (1 + Bn1 \cdot (T/Tc)) + (Bn2 \cdot (T/Tc)^2)$$

If I take only three terms  $n = 1, 2, 3$  of the volume dependence, the conditions for the critical isotherm at the critical point,  $pF(V_c, T_c) = p_c$ ,  $KF(V_c, T_c) = 0$ , and  $KFs(V_c, T_c) = 0$ , and the given values for  $p_c$ ,  $T_c$ , and  $V_c$  result in the following relations for the coefficients  $a_1$ ,  $a_2$ , and  $a_3$ :

$$a_1 = \frac{V_c}{2 \cdot R \cdot T_c} \cdot [12 \cdot (p_c - pFCc) + 7 \cdot KFcc + KKFCsc] - 3$$

$$a_2 = \frac{-V_c}{2 \cdot R \cdot T_c} \cdot [8 \cdot (p_c - pFCc) + 6 \cdot KFcc + KKFCsc] + \frac{3}{2}$$

$$a_3 = \frac{V_c}{6 \cdot R \cdot T_c} \cdot [6 \cdot (p_c - pFCc) + 5 \cdot KFcc + KKFCsc] - \frac{1}{3}$$

where  $pFCc$ ,  $KFCc$ , and  $KFCsc$  are the values of the pressure, bulk modulus and its pressure derivative of the hypothetical zero temperature isotherm at  $V_c$ . I should point out that these values depend on the parameters  $V_{Fo}$ ,  $K_{Fo}$ ,  $K_{fso}$ , which have to be determined by additional constraints given by the volume of the fluid along the melting curve. This means that I have the 3 parameters  $V_{Fo}$ ,  $K_{Fo}$ ,  $K_{fso}$ , which enter into the fit of the coefficients  $a_1$ ,  $a_2$ , and  $a_3$ , and at least the additional 3 parameters  $B_{11}$ ,  $B_{21}$ ,  $B_{31}$  when I fit the EOS data along the melting curve.

When data for the volume of the fluid along the melting curve are missing, EOS data for the solid can provide reasonable estimates. It is clear that this first order model with only 6 parameters to be fitted to experimental data gives only first estimates for the EOS of the fluid over wide ranges in pressure and temperature. However the present approach has good potential for future refinements, when more data are available. As a first test of the present model and its implication for the interpretation of experimental data I analyze data for argon.

### 3. Test of the model with data for argon

As most important input I use at first data for the critical point of argon:  $p_c = 4.898 \text{ MPa}$ ,  $T_c = 150.85 \text{ K}$ , and  $V_c = 1.872 \text{ cm}^3/\text{g}$  from the

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