

An Applicability Aspect of Quasi Harmonic Debye Model

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ABSTRACT

The quest for the nature of interatomic interactions in solids is of paramount importance as it leads to an understanding of their thermodynamical, elastic and numerous other physical properties. The thermodynamical properties either completely dictate the nature of the response of the materials or control the driving force for kinetic steps. The proposal presents an introduction to quasi harmonic Debye model and its applicability aspect in the understanding of thermodynamical, elastic and numerous other physical properties of wide range of materials.

I. INTRODUCTION

The equation of state (EOS) and the chemical potential are two of the key thermodynamic properties of a solid. The EOS of a given crystalline phase determines its behavior with respect to changes in the macroscopic variables, mainly pressure (p) and temperature (T). Experimental measurements are daily performed to determine the EOS of new materials or to extend it to wider p and/or T ranges. The results are usually expressed in terms of a reduced number of parameters by fitting the pressure-volume experimental data to an empirical equation. The chemical potential μ (equivalent to the molar Gibbs function, G_m) is the magnitude governing phase stability and change. Although its measurements are not so common, its effects in terms of phase transition properties and ranges of phase stability are some of the most important in state-of-the-art experimental solid state

science. On the theoretical side, the determination of the EOS and the chemical potential from first principles are also two of the main objectives of the Physics and Chemistry of crystals. To obtain them, one has to pay particular attention to the concept of thermodynamic equilibrium state. According to standard thermodynamics, if the system is held at a fixed T and suffers a constant and hydrostatic p , the equilibrium state is the one that minimizes the availability or non-equilibrium Gibbs energy of the crystal phase¹,

$G^*(x; p, T) = E(x) + pV(x) + A_{\text{vib}}(x; T)$
with respect to all internal configuration parameters. These configuration parameters, gathered in the configuration vector x , include all the relevant geometric information for the given crystal structure, i.e. the independent unit cell lengths and angles of this phase, and all the free crystallographic coordinates of the atoms in

non-fixed Wyckoff positions. On the right-hand side of above equation, $E(x)$ is the total (or cohesive, if we set the energy zero at the infinitely separated components) energy of the crystal, which corresponds to the potential energy surface as determined by most electronic structure or atomistic calculations. The second term, pV , corresponds to the constant hydrostatic pressure condition. Finally, the third term, A_{vib} , is the vibrational Helmholtz free energy, which includes both the vibrational contribution to the internal energy and the $-T S$ constant temperature condition term (since a perfect crystal is considered whose only internal degrees of freedom are vibrations, $S=S_{\text{vib}}$). The rigorous statistical calculation of A_{vib} requires knowledge of the exact vibrational levels, but it is customary to introduce the quasi-harmonic approximation¹,

$$A_{\text{vib}}(x; T) = \int_0^{\infty} \left[\frac{1}{2} \hbar \omega + kT \ln(1 - e^{-\frac{\hbar \omega}{kT}}) \right] g(x; \omega) d\omega$$

where $g(x; \omega)$ is the phonon or vibrational density of states. The term quasi-harmonic, as different from the rigid harmonic approximation, remarks that the density of states is allowed to vary with the crystal configuration, thus including anharmonic contributions to a certain extent.

Summarizing the above paragraph, a calculation of (p, T) equilibrium states requires knowledge of $E(x)$, $V(x)$, and $g(x; \omega)$. Since $V(x)$ can be readily computed for any given phase, and the potential energy surface is the main product of solid state computational codes, a first approach in which the vibrational effects (both finite-temperature and zero-point) are neglected is commonly used. In this static approach, the

static non-equilibrium Gibbs energy, $G^*_{\text{static}}(x; p) = E(x) + pV(x)$, is minimized with respect to x . Although the full minimization can usually be attained, in cases of high dimensionality and when using ab initio methods a restricted minimization can also be employed, for example fixing some of the internal parameters, cell angles, or ratios of cell lengths. Once G^*_{static} has been fully or partially minimized, the static EOS of the solid is recovered as $V(p) = V(x_{\text{opt}}(p))$, and its chemical potential as $G(p) = G^*_{\text{static}}(x_{\text{opt}}(p); p)$. Although these results are quite valuable and give good insights into the general behavior of crystalline phases, they are not comparable to the experimental results. Even for low T , thermal effects are present both in the form of zero point and finite temperature contributions, and their inclusion in the theoretical study of crystals is very relevant, not only when studying temperature dependences but also for fixed- T studies. Some methods have recently been developed to fully minimize $G^*(x; p, T)$ with respect to x within the quasi harmonic approximation when simple pair potentials are used in the crystal simulation^{2(a)}. However, when a first principles method is used, the full minimization of $G^*(x; p, T)$ is currently infeasible. This fact has motivated M.A. Blanco *et al.*^{2(b)} to develop a non-empirical model to include thermal effects in a general way after a possibly expensive calculation of the potential energy surface of a crystalline phase³⁻⁷. M. A. Blanco *et al.*^{2(b)} have thus made it work with a minimal amount of data, in this case a set of computed pairs of energies and volumes per unit formula, that correspond to the lowest energy configuration x_{opt} compatible with that volume. The simplicity of the requirements makes it completely general,

although it is expected to work better for highly symmetric crystals.

II. THE QUASI-HARMONIC DEBYE MODEL

Basic input of the model: static optimizations

Let us assume that an appropriate (ab initio⁸⁻¹² or otherwise) approximate algorithm to compute $E(x)$ is available. Then, before the quasi-harmonic Debye model can be properly applied, this multivariable surface has to be transformed into an $E(V)$ curve. This can be done in two equivalent ways. On the one hand, since the volume is usually a quite simple function of the lattice parameters, one can minimize $E(x)$ for a set of fixed volumes, for example, optimizing the internal coordinates, angles, and cell length ratios (c/a and b/a); writing $V = abcf(\alpha, \beta, \gamma)/Z = a^3g(\alpha, \beta, \gamma, b/a, c/a)$, where Z is the number of molecules per unit cell, and f and g depend on the crystal system and Bravais lattice of the phase, the last cell length is then univocally defined for each volume to be $a = [V/g(\alpha, \beta, \gamma, b/a, c/a)]^{1/3}$. This produces a curve $E(V) = E(x_{\text{opt}}(V))$ that contains the points of the surface which have lowest energy for different constant V hyperplanes. On the other hand, one can perform static optimizations at several constant pressures, using the $G^*_{\text{static}}(x;p) = H^*_{\text{static}}(x;p) = E(x) + pV(x)$ function to obtain $x_{\text{opt}}(p)$. As shown above in the introduction, this leads to the static EOS $V(p) = V(x_{\text{opt}}(p))$, and thus M. A. Blanco *et al.*^{2(b)} obtained $E(p) = E(x_{\text{opt}}(p))$. Since the EOS was a table of (V,p) values, they invert it to obtain (E,V) pairs, as they wanted. Both procedures are equivalent, since H^*_{static} is nothing but the Lagrange function for the

minimization of E at constant V , being p the corresponding Lagrange multiplier. Thus, both $E(V)$ curves are one and the same, and choosing one or the other of these procedures will only change the actual points selected from the single curve. Since, in what follows, the $E(V)$ curve is the key input data for several numerical minimization procedures, V points with a homogeneous distribution should be used, and they should span values both above and below the static zero-pressure equilibrium volume V_0 . Thus, if no previous information on the $V(p)$ EOS is available, fixed volume optimizations are preferred, selecting an appropriate volume grid. This avoids the selection of a pressure grid that should include unphysical negative pressures, in order to sample points above V_0 . An important word of caution should be given here. Since by selecting an univocal correspondence $x_{\text{opt}}(V)$ between configurations and volumes, given by the static calculation, M.A. Blanco *et al.*^{2(b)} effectively assumed that thermal effects over the configuration can be reduced to the thermal effects over volume. Having $x = x_{\text{opt}}(V)$ is the case in the static calculation, and usually holds for pressure-induced effects at constant temperature, too; it can even be a good approximation for temperature-induced effects, but this will only be true when the vibrational effects act as a hydrostatic term, i.e. are isotropic.

Thermal effects: quasi-harmonic Debye model

After the static calculation, the non equilibrium Gibbs function $G^*(V;P,T)$ can be written in the form of^{5,2(b)}
 $G^*(V;P,T) = E(V) + PV + A_{\text{vib}}(\Theta(V);T)$,
 where $E(V)$ is the total energy per unit cell, PV corresponds to the constant hydrostatic

pressure condition, and $A_{\text{vib}}(\Theta(V);T)$ is the vibrational term, which can be written as

$$A_{\text{vib}}(\Theta(V); T) = nKT \times \left[\frac{9\Theta}{8T} + 3 \ln \left(1 - e^{-\Theta/T} \right) - D(\Theta/T) \right]$$

where n is the number of atoms in the molecule, and the Debye integral $D(\Theta/T)$ is defined as^{2(b)}

$$D(y) = \frac{3}{y^3} \int_0^y \frac{x^3}{e^x - 1} dx.$$

For an isotropic solid, Θ is expressed by

$$\Theta = \frac{\hbar}{k} [6\pi^2 V^{1/2} n]^{1/3} f(\sigma) \sqrt{\frac{B_S}{M}}$$

where M is the molecular mass per formula unit, B_S the adiabatic bulk modulus, which can be approximated by the static compressibility^{2(b)}

$$B_S \sim B(V) = V \left(\frac{d^2 E(V)}{dV^2} \right)$$

and the Poisson ratio σ and $f(\sigma)$ ^{5,6]} are given by the following forms:

$$\sigma = \frac{3B - 2G}{6B + 2G}$$

$$[f(\sigma)]^3 = 3 \left[2 \left(\frac{2}{3} \frac{1 + \sigma}{1 - 2\sigma} \right)^{3/2} + \left(\frac{1}{3} \frac{1 + \sigma}{1 - \sigma} \right)^{3/2} \right]^{-1}$$

Therefore, the non-equilibrium Gibbs function $G^*(V;P,T)$ as a function of $(V;P,T)$ can be minimized with respect to volume:

$$\left[\frac{\partial G^*(V;P,T)}{\partial V} \right]_{P,T} = 0 \quad (1)$$

The isothermal bulk modulus B_T , the heat capacity C_V and the thermal expansion coefficient (α) are expressed as^{2(b)}

$$B_T(P, T) = V \left[\frac{\partial^2 G^*(V; P, T)}{\partial V^2} \right]_{P,T}$$

$$C_V = 3nk \left[4D(\Theta/T) - \frac{3\Theta/T}{e^{\Theta/T} - 1} \right]$$

$$\alpha = \frac{\gamma C_V}{B_T V}$$

where γ is the Gruneisen parameter defined as

$$\gamma = - \frac{V \ln \Theta(V)}{d \ln V}$$

III. COMPUTATIONAL SCHEME

To simplify the process of minimization/derivation involved in the above equations, it is convenient to fit an appropriate analytical function of V to the numerical values of $G^*(V;T,p)$ and $E(V)$. Since typical energy curves resemble anharmonically distorted parabolae, simple polynomials in V are commonly used. However, this possibility leads to large errors in the values of the fitted function, specially at high volumes. To minimize these errors, instead of V , M.A. Blanco *et al.*^{2(b)} used the reduced length unit $x = (V/V_{\text{ref}})^{1/3}$, where V_{ref} is chosen as the value of V in the (E,V) table for which E is a minimum. Even with this improvement, the derivatives obtained were highly dependent on the polynomial order and on the end point values of the data set. To avoid this problem, they fit polynomials with a wide range of orders, and successively redo the fitting eliminating the endpoints from the input data. In this way, get a large number of different polynomials to estimate $G^*(V;T,p)$. Then, they averaged the fittings, assigning to the i^{th} polynomial a weight equal to $p_i = e^{-\omega_i^2} / \sum_i e^{-\omega_i^2}$, where $\omega_i = [(n_i + 1)/N_i][\delta_i/\delta_{\text{min}}]$ n_i is the polynomial degree, N_i the number of (E,x) data, δ_i is the root mean square deviation in the i^{th} fitting, and $\delta_{\text{min}} = \min\{\delta_i\}$. In this way, they^{2(b)} obtained numerically stable values for both the minimum of the function

and its successive derivatives, while retaining the simplicity of the polynomial fittings.

The above fitting strategy was applied both to the static (E,x) data and to the thermal (A*,x) data (A*(V;T) = E(V)+A_vib(Θ(V);T)). It is worth mentioning that only the zero-pressure data at each T need to be fitted. Indeed, if $f(x) = \sum_i a_i x^i$ is the polynomial that best fits the (E,x) data, the best polynomial fitting for the (E + pV,x) data with $p \neq 0$ coincides with it after changing the third-order coefficient to $a_3' = a_3 + pV_{ref}$. This is evident when considering that $pV = px^3 V_{ref}$. Once the E(x) function has an analytical form, Θ(x) can be obtained by simple analytical derivation of the polynomial, and the (A*(x;T),x) data obtained. The fitting strategy then provided them^{2(b)} with the G*(x;p,T) polynomial function for any selected temperature and pressure. Then, solving Eq. (1) by a combination of bisection in the (G*, x) data and the Newton–Raphson method, since both the first derivative (the function to be zeroed) and the second derivative (the derivative of the function to be zeroed) are polynomials easy to obtain from the original G*(x) one. A further auxiliary polynomial fit was performed with the lnΘ versus lnV values, both as a means of accessing Θ at values other than those in the input, and as a means of obtaining the Grüneisen parameter.

IV. EMPIRICAL ANALYTICAL EOS

The Gibbs program can fit analytical expressions to the p(V) data obtained by solving Eq. (1). These empirical EOS involve the zero-pressure bulk modulus, B₀, and its first, second, . . . pressure derivatives (B₀['], B₀^{''}, . . .) as fitting parameters, thus providing an alternative derivation of the

compressibility. These analytical expressions can easily be manipulated to derive most thermodynamic properties at any T and p. The static analytical EOS can be likewise used to compute Θ(V) after a corresponding fit to the static p(V) values. As a means of estimating the quality of the EOS fitting, the explicit p(V) expressions can be analytically integrated to obtain the corresponding energy (E in the static calculations, or the Helmholtz non-equilibrium energy function A* in the thermal calculations), which can then be directly compared with the original energy volume data. Presently, three possibilities are incorporated in Gibbs: the Vinet *et al.* EOS¹⁴, the Birch–Murnaghan EOS¹³, and the spinodal EOS¹⁵.

The Vinet EOS

This EOS connects the p(V) data through the relation

$$\ln[px^2/3(1-x)] = \ln B_0 + a(1-x),$$

$$x = (V/V_0)^{1/3}$$

where V₀ = V(0,T) is the zero pressure equilibrium volume and ln B₀ and a = 3(B₀['] - 1)/2 are the fitting parameters.

$$B_T = -x^{-2} B_0 e^{a(1-x)} f(x)$$

$$B_T' = \left(\frac{\partial B_T}{\partial p}\right)_T = 1/3[(ax + 2)$$

$$-x f(x)/f(x)], \quad \text{and} \quad B_T'' = \left(\frac{\partial^2 B_T}{\partial p^2}\right)_T =$$

$$x/9B_T \left\{ x \frac{f''(x)}{f(x)} - a + \frac{f'(x)}{f(x)} \left[1 - \right.$$

$$\left. x \frac{f'(x)}{f(x)} \right] \right\} \text{ where } f(x) = x - 2 - ax(1-x).$$

The Birch Murnaghan EOS

In the second order Birch Murnaghan EOS the p(V) data are connected by the equation

$$F(f) = \frac{p}{3f(1+2f)^{5/2}} = \sum_{i=0}^2 a_i f^i,$$

where $f=1/2(x^2-1)$ (x having the same meaning as in the Vinet EOS), and a_0 , a_1 , and a_2 are fitting parameters. The expressions for B_T , B_T' and B_T'' at zero pressure values are given by

$$\begin{aligned} B_0 &= a_0 \\ B_0' &= 4 + (2a_1/3B_0) \\ B_0'' &= \left[\frac{2a_2}{3B_0} - B_0'(B_0' - 7) - \left(\frac{143}{9} \right) \right] / B_0 \end{aligned}$$

The spinodal EOS

The spinodal EOS proposed by Baonza *et al.*¹⁵ connects the (p,V) data through the relation

$$V_L = V_{sp} \exp \left\{ - \left[\frac{K^*}{1-\beta} \right] (p - p_{sp})^{1-\beta} \right\}$$

where

$$V_{sp} = V_0 \exp \left\{ \frac{\beta}{(1-\beta)B_0'} \right\}$$

In the above equation, p_{sp} and v_{sp} are the spinodal pressure and volume respectively. The fitting parameters are p_{sp} , K^* , and β (it is customary to use $\beta=0.85$). In terms of them, we have

$$\begin{aligned} B_0 &= [K^*]^{-1} (-p_{sp})^\beta \\ B_0' &= (-p_{sp})^{-1} \beta B_0 \end{aligned}$$

At any T and p , B_T , B_T' and B_T'' are straightforwardly given by

$$\begin{aligned} B_T &= [K^*]^{-1} (p - p_{sp})^\beta \\ B_T' &= \beta [K^*]^{-1} (p - p_{sp})^{\beta-1} \\ B_T'' &= \beta(\beta - 1) [K^*]^{-1} (p - p_{sp})^{\beta-2} \end{aligned}$$

The expression of B_T is the one used to optimize $(-p_{sp})$, K^* , and β from the B_T values. Putting it in the form

$$\ln B_T = \beta \ln(p - p_{sp}) - \ln K^*$$

And given a trial value of $(-p_{sp})$ and the set of data (p, B_T) , K^* and β are obtained solving the corresponding linear least squares problem. The optimum $(-p_{sp})$ is trivially found by a monodimensional minimization.

V. OTHER THERMODYNAMIC PROPERTIES

After the equilibrium state for a given (p,T) has been obtained, other thermodynamic properties can also be evaluated by using the corresponding equilibrium volume in the appropriate thermodynamic expressions. For instance, the vibrational internal energy (U_{vib}), heat capacity ($C_{v,vib}$), and entropy (S_{vib}) in the quasi-harmonic Debye model are given by^{2(b)}

$$U_{vib} = nKT \left[\frac{9}{8} \frac{\Theta}{T} + 3D \left(\frac{\Theta}{T} \right) \right]$$

$$C_{v,vib} = 3nk \left[4D \left(\frac{\Theta}{T} \right) - \frac{3}{e^{\Theta/T} - 1} \frac{\Theta/T}{T} \right]$$

$$S_{vib} = nk \left[4D \left(\frac{\Theta}{T} \right) - 3 \ln \left(1 - e^{-\Theta/T} \right) \right]$$

Another relevant property is the Grüneisen parameter, defined as

$$\gamma = - \frac{V \ln \Theta(V)}{d \ln V}$$

The only explicit dependence of this parameter is on V . However, since the derivative must be evaluated at the equilibrium volume at each T and p , it has an implicit dependence on these two variables. Although the above equation can be used directly to obtain γ , it is more

accurate to derive it from the Mie–Grüneisen equation

$$p - p_{\text{static}} = \gamma \frac{U_{\text{vib}}}{V}$$

The second member of this equation represents the thermal contribution to the pressure. Finally, the thermal expansion (α), the heat capacity at constant pressure ($C_{p,\text{vib}}$), and the adiabatic bulk moduli are given by^{2(b)}:

$$\alpha = \frac{\gamma C_{v,\text{vib}}}{B_T V}$$

$$C_{p,\text{vib}} = C_{v,\text{vib}}(1 + \alpha \gamma T)$$

$$B_S = B_T(1 + \alpha \gamma T)$$

ACKNOWLEDGEMENT

Authors acknowledge thanks due to all departmental researchers and teachers.

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