Intrinsic Anharmonicity in Equations of State of Solids and Minerals

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Intrinsic anharmonicity plays an important role in equations of state of minerals intended for the calculation of thermodynamic functions under conditions of the Earth’s mantle. The simplest method for taking intrinsic anharmonicity into account was proposed by Zharkov and Kalinin, who expressed the anharmonicity-related free energy as

\[ F_a(V, T) = \frac{3}{2} n Ra T^2 = \frac{3}{2} n Ra_0 x^m T^2, \quad (1) \]

where \( n \) is the number of atoms in a unit cell, \( R \) is the gas constant, \( x = V/V_0 \), \( a_0 \) is the anharmonicity parameter under the starting conditions, and \( m = (\partial \ln a / \partial \ln V)_T \) [3]. The dependence \( F_a \sim T^2 \) follows from the first-order thermodynamic perturbations theory. Model (1) also assumes an exponential dependence of the anharmonicity parameter on the volume: \( a = a_0 x^m \).

Thus, the contribution of anharmonicity to the entropy, intrinsic energy, heat capacity, pressure, isothermal bulk modulus, and pressure slope can be written at constant volume as

\[ S_a = -3nRaT, \quad E_a = \frac{3}{2} \cdot 3nRaT^2, \]
\[ C_{V_a} = -3nRaT, \]
\[ P_a = \frac{3}{2} n Ra_0 m x^m T^2, \quad K_{Ta} = P_a(1 - m), \quad (2) \]
\[ \left( \frac{\partial P}{\partial T} \right)_{V_a} = \frac{mC_{V_a}}{V}. \]

We applied this very efficient system for high temperatures in [2, 7]. At low temperatures, however, the linear anharmonic term (2) begins to dominate the heat capacity (the sum of the quasi-harmonic and anharmonic contributions). This circumstance adversely affects the thermal expansion coefficient and Gruneisen parameter \( \Gamma = \alpha V K_T / \Theta_V \) in the region below 100 K.

The problem is that classical expressions (1) and (2) do not take into account quantum effects that determine the low-temperature behavior of thermodynamic functions. If these effects are taken into account, for Debye crystals at low temperatures, we obtain \( C_{V_a} \sim T^4 \) rather than \( C_{V_a} \sim T \), as would follow from classical formula (2). Let us consider how one can take into account quantum effects that determine thermodynamic functions at low temperatures into account.

QUASI-HARMONIC MODELS
WITH A CORRECTION FOR INTRINSIC ANHARMONICITY

Intrinsic anharmonicity reflects the fact that the characteristic temperature depends not only on volume but on temperature as well. A temperature correction can be introduced into the characteristic temperature by various methods (see, for example, [5–6, 8–9, 11]). It is convenient to determine the intrinsic anharmonicity parameter as a logarithmic derivative of the vibrational frequencies \( \omega \) (or, equivalently, the characteristic temperature \( \Theta \)) with respect to temperature:

\[ a = \left( \frac{\partial \ln \omega(V, T)}{\partial T} \right)_V = \left( \frac{\partial \ln \Theta(V, T)}{\partial T} \right)_V, \quad (3) \]

and parameter \( m \):

\[ m = \frac{d \ln a}{d \ln V}. \quad (4) \]

Then, the characteristic temperature at \( V \) and \( T \) is

\[ \Theta(V, T) = \Theta(V) \exp(aT) = \Theta(V) \exp(a_0 x^m T), \quad (5) \]

where \( a_0 \) and \( m \) are constants to be determined. In the quasi-harmonic approximation, we neglect the \( \Theta-T \) dependence; i.e., the exponential factor is absent in (5).

According to Wallace, the use of the quasi-harmonic expression for the entropy

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The equation of state can be constructed taking into account anharmonically renormalized characteristic temperature (5), produces correct (to first-order in anharmonicity) [12]. Expressions (1) and (2) are derived from (8) as contributions of anharmonicity in the classical limit \((\Theta/T \rightarrow 0)\). At very high temperatures, third- and fourth-order anharmonic terms also become significant in the Helmholtz free energy. However, they are not taken into account in [12].

Then, all the other thermodynamic functions (for example, isochoric heat capacity and the pressure–temperature slope for the constant volume) can be obtained from the entropy:

\[
\begin{align*}
C_V &= T \left(\frac{\partial S}{\partial T}\right)_V \\
&= \left(\frac{\Theta(V, T)}{T}\right)^2 \exp(\Theta(V, T)/T) \left(\frac{\exp(\Theta(V, T)/T)}{\exp(\Theta(V, T)/T) - 1}\right)^2 (1 - aT), \\
\frac{\partial P}{\partial T}_V &= \frac{\partial S}{\partial V}_T \\
&= \left(\frac{\Theta(V, T)}{T}\right)^2 \frac{\exp(\Theta(V, T)/T)}{\exp(\Theta(V, T)/T) - 1} (\gamma - amT). \tag{7}
\end{align*}
\]

Let us find the intrinsic energy \(E\) by integration of the heat capacity (7) and, then, the Helmholtz free energy \(F = E - TS\). The thermal pressure is found by the integration of (8) or differentiation of the Helmholtz free energy (see [8]). Unfortunately, functions (7) and (8) cannot be analytically integrated. This circumstance does not hamper the construction of the equation of state, but introduces some difficulties into the thermodynamic calculations.

An approach where one begins to construct the equation of state not from the entropy, as in [12] (hereinafter, the S-EoS model), but from the Helmholtz free energy (hereinafter, the F-EoS model), as in the overwhelming majority of studies (for example, [1, 5–7, 9]), is of great interest. This inevitably yields thermodynamic functions that are different from those in [12]. Therefore, it is very important to find out how different are the results of these two approaches.

In the F-EoS model, the characteristic temperature should be written as

\[\tilde{\Theta} = \Theta(V, T) = \Theta(V) \exp\left(\frac{1}{2} a \Theta^m T\right), \tag{9}\]

where the factor 1/2 is introduced into the exponent to obtain correct classical limits (1) and (2). Now, the equation of state can be constructed taking into account the intrinsic anharmonicity in the analytic form by a simple differentiation of the Helmholtz free energy. For simplicity, we shall consider the Einstein model. Then, the contributions of heat oscillations into the Helmholtz free energy and all the other functions without the factor \(3nR\) appear as:

\[
F = \frac{1}{2} \Theta(V) + T \ln(1 - \exp(-\tilde{\Theta}/T)). \tag{10}
\]

\[
S = - \ln(1 - \exp(-\tilde{\Theta}/T)) + \frac{\tilde{\Theta}}{T(\exp(\tilde{\Theta}/T) - 1)} \times \left(1 - \frac{1}{2} a T\right). \tag{11}
\]

\[
E = \frac{1}{2} \Theta(V) + \frac{\tilde{\Theta}}{\exp(\tilde{\Theta}/T) - 1} \left(1 - \frac{1}{2} a T\right), \tag{12}
\]

\[
C_V = \left(\frac{\tilde{\Theta}}{T}\right)^2 \frac{\exp(\tilde{\Theta}/T)}{\exp(\tilde{\Theta}/T) - 1} \times \left(1 - \frac{1}{2} a T\right) - \frac{1}{4} a^2 T \tilde{\Theta} \frac{\exp(\tilde{\Theta}/T)}{\exp(\tilde{\Theta}/T) - 1}, \tag{13}
\]

\[
P = \frac{1}{2} \gamma \frac{\Theta(V)}{V} + \frac{\tilde{\Theta}}{V(\exp(\tilde{\Theta}/T) - 1)} \times \left(\gamma - \frac{1}{2} a \tilde{T}\right), \tag{14}
\]

\[
K_T = P - \frac{\gamma \Theta(V)}{2V} (q - 1) \tilde{\Theta} \left(\gamma - \frac{1}{2} a \tilde{T}\right) \frac{\exp(\tilde{\Theta}/T)}{V(\exp(\tilde{\Theta}/T) - 1)} - \frac{\exp(\tilde{\Theta}/T)}{V(\exp(\tilde{\Theta}/T) - 1)}, \tag{15}
\]

\[
\frac{\partial P}{\partial T}_V = \frac{\frac{1}{2} a \tilde{\Theta} \left(\gamma - m - \frac{1}{2} a \tilde{T}\right)}{V(\exp(\tilde{\Theta}/T) - 1)} + \frac{\tilde{\Theta}^2 \left(\gamma - \frac{1}{2} a \tilde{T}\right) \left(1 - \frac{1}{2} a \tilde{T}\right) \exp(\tilde{\Theta}/T)}{T^2 V(\exp(\tilde{\Theta}/T) - 1)^2}. \tag{16}
\]

It is easy to see that the anharmonic contributions in (10)–(16) reduce to (1) and (2) in the classical limit. It is easy to generalize these relationships into the Bose–Einstein free energy approximation [4]. Note that in formulas (10), (12), (14), and (15), we have ignored the anharmonic contribution to the zero-point energy and used only the harmonic zero-point energy that exceeds the anharmonic term by two to three orders of magnitude.
Let us compare S-EoS and F-EoS models using MgO as example. For MgO, intrinsic anharmonicity was estimated from \emph{ab initio} calculations \cite{10}: \( a_0 = (17.71–19.69) \cdot 10^{-6} \text{ K}^{-1} \) and \( m = 5 \). Let us further accept that \( a_0 = 20 \cdot 10^{-6} \text{ K}^{-1} \), \( \gamma = 1.5 \), and \( m = 5 \) and compare a number of functions at constant volume with \( \Theta_0 = 1000 \text{ K} \).

Figure 1 shows the difference between the entropy, heat capacity, and pressure calculations based on the S-EoS and F-EoS models and the classical model. The difference in the entropy reaches 1% at low temperatures and decreases to 0.3% at high temperatures. The lower the characteristic temperature or intrinsic anharmonicity, the less the difference. These differences in heat capacity are several times lower, except in the low-temperature region. The difference in thermal pressure amounts to nearly 1% at low temperatures and almost linearly increases to 1.3% at high temperatures. The differences in the thermal part of the bulk modulus are greater (~8% at 4000 K and as much as 100% at low temperatures). However, since the thermal contribution to the bulk modulus is small, this difference almost does not affect the total bulk modulus. The same is true for the thermal expansion coefficient, for which the differences will be less than 2% at 4000 K and negligible at low temperatures. Under compression, the intrinsic anharmonicity parameter sharply decreases and both models become similar to the quasi-harmonic Einstein model. The classical model and the S-EoS model are very close to each other at high temperatures. However, the differences in \( S, \ C_v \) and \( P \) exceed 100% at temperatures below 200 K.

Figure 2 shows the anharmonic part of the heat capacity based on the classical model (2) and on S-EoS and F-EoS models with \( \Theta_0 = 1000 \text{ K} \). The S-EoS and F-EoS models provide a correct variation pattern of anharmonic heat capacity at low temperatures, although the anharmonic heat capacity near 0 K differs from these models by a factor of two. This difference rapidly decreases with increasing temperature. At high temperatures, all three models provide quite similar anharmonic contributions to the heat capacity. Figure 2 also shows that if one uses the classical model for intrinsic anharmonicity, then the total heat capacity (sum of the quasi-harmonic and anharmonic heat capacities) becomes negative at low temperatures, which contradicts the theory. The consideration of the quantum corrections according to the S-EoS and F-EoS models eliminates this contradiction.

Thus, we have considered two approaches to intrinsic anharmonicity. The aforesaid approaches to intrinsic anharmonicity are all applicable to solid bodies only. They assume weak anharmonicity, i.e., \( aT \ll 1 \). Otherwise, at very high temperatures the parameter \( \frac{\Theta}{T} = \frac{\Theta(V)e^{aT}}{T} \) would increase (instead of decreasing) and a nonphysical departure from the classical limit will take place at very high temperatures. We can recommend these approaches at \( aT \leq 0.05 \), which corresponds to temperatures of up to several thousand Kelvin for most minerals. This interval will increase with pressure growth due to a rapid decrease in parameter \( a \) with compression.

**CONCLUSIONS**

Thus, we have considered two approaches to the construction of equations of state including intrinsic anharmonicity. Entropy is the primary function in the Wallace model \cite{12}, whereas the Helmholtz free energy is primary in the standard F-EoS model. The expressions for thermodynamic functions are different in these models. The differences in the total thermodynamic
functions can reach 1.5–2%, depending on conditions. Nevertheless, all the classical limits are fulfilled in the standard model. Therefore, such equations of state can be used in the analysis of PVT relationships of solids and minerals.

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