

Physical contradictions and remedies using simple polythermal equations of state

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ABSTRACT

Simple polythermal extensions to two widely used isothermal equations of state, the Murnaghan and the Birch-Murnaghan, can lead to non-physical material behavior without proper parameterization: the thermal expansivity at high pressure can become negative. We show how this arises and propose a remedy using an approximation to the thermal relaxation of the bulk modulus. Using the revised equation of state for thermodynamic equilibrium calculations leads to low-pressure and -temperature behavior indistinguishable from the unmodified equation of state, yet extrapolates to high pressure and temperature without non-physical behavior.

Keywords: Thermodynamics, equation of state properties, phase equilibria, calculation, high-pressure studies, expansivity measurements, negative expansivity

INTRODUCTION

Phase equilibrium calculations are routine practice for metamorphic petrologists (e.g., Schumacher et al. 2008) and coming into vogue for the calculation of seismic wavespeeds in structural studies of the mantle and core (Sobolev and Babeyko 1994; Connolly and Kerrick 2002; Helffrich and Kaneshima 2004; Stixrude and Lithgow-Bertelloni 2005; Richard et al. 2005). One reason for this is the development and packaging of efficient algorithms for phase equilibrium calculation that employ simply parameterized equations of state (Holland and Powell 1998). Phase equilibrium is typically calculated using the deviation of free energy, dG , from reference temperature T and pressure P conditions (T_r, P_r) via

$$G(P, T) = G(P_r, T_r) + \int_{P_r}^P V(p) dp - \int_{T_r}^T S(t) dt \quad (1)$$

where the first integral involving volume (V) is done isothermally and the second involving entropy (S), isobarically. Due to the wealth of 1 bar thermophysical property measurements, the T integral is usually done at $P_r = 1$ bar. This requires the P integral to be done at T . Consequently, there is a need for $V(T)$ at 1 bar, as well as volume equation of state parameters usable at high T .

For fixed bulk composition, equilibrium calculations are based on the scalar function $G(P, T)$. Once G is calculated, the stable phase assemblage may be found by minimizing G subject to the bulk composition constraint. At that point, both the constituent mineral properties and the system properties may be found from G using various thermodynamic identities. For example, because V is $(\partial G / \partial P)_T$, numerical or analytic derivatives of G yield the volumes. Of especial interest in this family

of properties is the thermal expansivity, $\alpha = (1/V)(\partial V / \partial T)_P$, which may be obtained from phase or system properties via

$$V\alpha(P, T) = (\partial V / \partial T)_P = \left[\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial P} \right)_T \right]_P. \quad (2)$$

This represents the high-pressure and -temperature expansivity. Continuum theories of material behavior posit a positive-definite strain energy function to define material mechanical stability. The strain tensor, E_{ij} , includes a thermal component through α

$$E_{ij} = \left[\alpha(T - T_0) - \frac{\nu}{E} \sigma_{kk} \right] \delta_{ij} + \frac{1 + \nu}{E} \sigma_{ij} \quad (3)$$

(summation convention used)

and also depends on the material parameters Poisson's ratio ν , Young's modulus E , and stress tensor σ_{ij} (δ_{ij} is the Kronecker delta symbol). The work dW done by straining a material is (Malvern 1969)

$$dW = -PdE_{kk} + \sigma_{ij} dE_{ij} \text{ (summation convention used)}. \quad (4)$$

If α were negative at any pressure, thermal energy added to the substance would derive work from it. One could alternatively say that adiabatic compression of the material would cool it: planetary interiors could be colder than their surfaces in absent internal heat sources. This is non-geophysical behavior, though some substances exhibit negative α due to geometric peculiarities at low pressures and temperatures (Pryde et al. 1996).

We show that this form of non-physical behavior can arise if the thermal part of the volume equation of state is not integrated properly with the compression part of the equation of state. Examples and a straightforward remedy based on an observa-

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tionally justified approximation to simultaneous high- P and $-T$ mineral behavior follow.

PROBLEM STATEMENT

Typical choices for the volume equation of state (EOS) are the Murnaghan and Birch-Murnaghan (Poirier 1991). The two involve the bulk modulus,

$$K_{S/T} = -V \left(\frac{\partial P}{\partial V} \right) \quad (5)$$

where S/T denotes either adiabatic or isothermal conditions as appropriate. This definition itself constitutes a simple, but not very good, volume EOS by integration assuming constant bulk modulus, K . The Murnaghan and Birch-Murnaghan EOSs are successive refinements to the constant bulk modulus approximation. The Murnaghan EOS adopts the reasonable physical assumption that squeezed material resists more squeezing due to increased repulsive forces between the atoms comprising a substance. Thus K_T increases linearly with pressure with scale factor $K' = dK_T/dP$. The Birch-Murnaghan EOS elaborates on the same idea using finite strain to better account for high compressions at high P .

Both EOSs are typically isothermal. From Poirier (1991) Equation 4.7,

$$V(P) = V_r \left(1 + \frac{K'}{K_T} P \right)^{-1/K'} \quad (6)$$

Adding the thermal component to V_r and K_T and neglecting the effect of temperature on K' , which is small (Anderson and Isaak 1993), yields

$$V(P,T) = V(T) \left[1 + \frac{K'}{K_T(T)} P \right]^{-1/K'} \quad (6')$$

An obvious parameterization of $K_T(T)$ is to assume it declines linearly, with constant dK_T/dT , as theory and laboratory observations suggest (Born and Huang 1954; Isaak et al. 1998), and as many compilations employ (Fei and Saxena 1990; Sobolev and Babeyko 1994; Gerya et al. 2004; Mattern et al. 2005). Taking the high-pressure temperature derivative of Equation 6' as specified by Equation 2,

$$\begin{aligned} \frac{\partial V}{\partial T} &= \frac{-V(T)}{K'} \left[1 + \frac{K'}{K_T(T)} P \right]^{-1/K'} - 1 \left[\frac{-K' P}{K_T(T)^2} \frac{dK_T}{dT} \right] + \\ &\alpha V(T) \left[1 + \frac{K'}{K_T(T)} P \right]^{-1/K'} \end{aligned} \quad (7)$$

We seek a zero to this expression to show that, at some point, the EOS leads to negative α . Setting the left-hand side to zero, noting that $V(T)$ is strictly positive and that

$$\left[1 + \frac{K'}{K_T(T)} P \right]^{-1/K'}$$

is also strictly positive when $K_T(T) > 0$, this simplifies to

$$0 = \frac{1}{K'} \left[1 + \frac{K'}{K_T(T)} P \right]^{-1} \left[\frac{K' P}{K_T(T)^2} \frac{dK_T}{dT} \right] + \alpha \quad (8)$$

Solving for the pressure P_z when α is zero (going negative)

$$P_z = \frac{-\alpha K_T}{\frac{1}{K_T} \frac{dK_T}{dT} + \alpha K'} \quad (9)$$

For insight into the severity of the problem, take α to be a constant α_0 . $(dK_T)/(dT)$ will be strictly negative, so the requirement that P be positive leads to

$$\frac{dK_T}{dT} < -\alpha_0 K' K_T \quad (10)$$

For $\alpha_0 K' \approx 10^{-4} \text{ K}^{-1}$, $K_T \approx 10^6$ bars, a negative α is virtually guaranteed for typical $(dK_T)/(dT)$ values, which are usually a few hundred bars/K (Holland and Powell 1998).

A similar treatment may be applied to the Birch-Murnaghan equation, but with more algebraic work and less insight. The isothermal Birch-Murnaghan equation is (Poirier 1991, Eq. 4.41)

$$P = 3K_T f(1 + 2f)^{5/2}(1 + \phi f) \quad (11)$$

The finite strain $f = 1/2[(V_r/V)^{2/3} - 1]$ and $\phi = 3(K' - 4)/4$. Adding polythermal behavior explicitly,

$$P = 3 K_T(T) f(1 + 2f)^{5/2}(1 + \phi f) \quad (11')$$

with f now denoting finite strain relative to $V(T)$. Evaluating the desired derivative by chain rule yields

$$\frac{\partial V}{\partial T} = \frac{dV}{dP} \frac{\partial P}{\partial T} = -\frac{V}{K_T} \frac{dP}{dT} \quad (12)$$

which requires only an expression for dP/dT . Using the results (not derived for brevity) that $df/dV = -(1 + 2f)/(3V)$ and $df/dT = (df/dV)(dV/dT) = 2\alpha(1 + 2f)/3$, we write

$$\begin{aligned} \frac{dP}{dT} &= \frac{dK_T}{dT} 3f(1 + 2f)^{5/2}(1 + \phi f) + \frac{df}{dT} 3K_T \times \\ &\quad \left[(1 + 2f)^{5/2}(1 + \phi f) + 5f(1 + \phi f)(1 + 2f)^{3/2} + f(1 + 2f)^{5/2}\phi \right] \\ &= \frac{dK_T}{dT} \frac{P}{K_T} + 2\alpha K_T(1 + 2f) \times \\ &\quad \left[(1 + 2f)^{5/2}(1 + \phi f) + 5f(1 + \phi f)(1 + 2f)^{3/2} + f(1 + 2f)^{5/2}\phi \right]. \end{aligned} \quad (13)$$

Substituting Equation 13 into Equation 12 yields the desired expression

$$\begin{aligned} \frac{dV}{dT} &= -\frac{PV}{K_T^2} \frac{dK_T}{dT} - 2\alpha V(1 + 2f) \times \\ &\quad \left[(1 + 2f)^{5/2}(1 + \phi f) + 5f(1 + \phi f)(1 + 2f)^{3/2} + f(1 + 2f)^{5/2}\phi \right]. \end{aligned} \quad (14)$$

Setting the left-hand side to zero and solving for P_z , and dividing out the always positive V yields the pressure at which the thermal expansivity becomes zero:

$$P_z = -2\alpha K_T^2 \left(\frac{dK_T}{dT} \right)^{-1} (1 + 2f) \times O(1) \text{ terms} \quad (15)$$

for mantle strains, where $f \leq 0.1$. For $dK_T/dT \approx -2 \times 10^2$ bars/K, $\alpha \approx 3 \times 10^{-5}$ K $^{-1}$ and $K_T \approx 10^6$ bars, α becomes zero at about 30 GPa, a planetary pressure range plausibly encountered in phase equilibrium calculations.

ALTERNATIVE PARAMETERIZATION

The negative α arises due to the constant negative dK_T/dT . An alternative bulk modulus thermal dependence comes from the Anderson-Grüneisen parameter, defined as

$$\delta_T = \frac{-1}{\alpha K_T} \left(\frac{\partial K_T}{\partial T} \right)_p \quad (16)$$

and is approximately a constant (Anderson and Isaak 1993). For a quasi-harmonic parameter $q = 1$, Anderson and Isaak (1993) find that $\delta_T = K$, and that δ has no dependence on compression. This approximation may be usefully combined with the Murnaghan equation for a simple equation of state good for pressures to mid-Earth conditions when strains exceed the Murnaghan equation's applicability. Rather than $K_T(T) = K_{T0} + (dK_T/dT)(T - T_r)$, use Equation 16 to infer that

$$K_T(T) = K_{T0} \exp \left[-\delta_T \int_{T_r}^T \alpha(t) dt \right] \quad (17)$$

showing that K_T decays exponentially with T at a rate proportional to the volumetric expansion of the mineral with T . This in turn suggests that the instantaneous dK_T/dT is always negative but approaches zero at high T . Also of service is another relation that follows from the definition of δ_T ,

$$\frac{dK_T}{dT} = -\alpha \delta_T K_T. \quad (18)$$

Proceeding as before to examine the possibility of $\alpha(P, T)$ becoming negative, form an expression for $\partial V/\partial T$ at high pressure:

$$\left(\frac{\partial V}{\partial T} \right)_p = \frac{-V(T)}{K'} \left[1 + \frac{K'}{K_T(T)} P \right]^{-1} \times \left[\frac{-K' P}{K_T(T)^2} \right] \left[-K_T(T) \alpha \delta_T \right] + \alpha V(T) \left[1 + \frac{K'}{K_T(T)} P \right]^{-1}. \quad (19)$$

We seek a zero to this expression to show that at some point the EOS leads to negative α . Setting the left-hand side to zero, noting that $V(T)$ and zero pressure α are strictly positive, and also noting that

$$\left[1 + \frac{K'}{K_T(T)} P \right]^{-1}$$

is strictly positive, this simplifies to

$$0 = \frac{-P \delta_T}{K_T(T)} \left[1 + \frac{K'}{K_T(T)} P \right]^{-1} + 1. \quad (20)$$

Solving for P_z where $\alpha(P, T)$ equals zero,

$$P_z = \frac{K_T(T)}{\delta_T} \left[1 + \frac{K'}{K_T(T)} P \right] \quad (21)$$

which rearranges as

$$P_z = \frac{K_T(T)}{\delta_T} \left(1 - \frac{K'}{\delta_T} \right)^{-1} = \frac{K_T(T)}{\delta_T - K'}. \quad (22)$$

If $\delta_T = K'$ as initially assumed, at no finite pressure will $\alpha(P, T)$ be zero. For brevity, we call this the modified Murnaghan EOS.

Because a good approximation to δ_T is already available in thermodynamic compilations, either through explicit tabulation (Fei and Saxena 1990; Sobolev and Babeyko 1990; Gerya et al. 2004; Helffrich and Kaneshima 2004; Mattern et al. 2005) or assuming that for all substances $K' \approx 4$ (Holland and Powell 1998), whence $\delta_T \approx 4$, one can employ the modified Murnaghan EOS without change to existing mineral thermophysical property compilations. If δ_T is available and exceeds K_T , the difference is unlikely to exceed unity (Anderson et al. 1992). Thus P_z will be on the order of K_T , $\sim 10^6$ bars, a pressure that invalidates Murnaghan EOS use.

As a concrete example, Figure 1 shows phase equilibria for the system $K_2O-Al_2O_3-SiO_2$ at high pressures calculated using the Murnaghan and the modified Murnaghan EOS. Yong et al. (2006) refined the thermodynamic data for the phases K-hollandite and Si-wadeite that we show calculated with the Perple_X program (Connolly 2005). Thermophysical data relevant to phase volumetric properties are listed in Table 1.

With the exception of hollandite and wadeite, the differences calculated by either EOS are small (Fig. 1). Using Equation 9 and the wadeite data in Table 1, the negative $\alpha(P, T)$ onset at

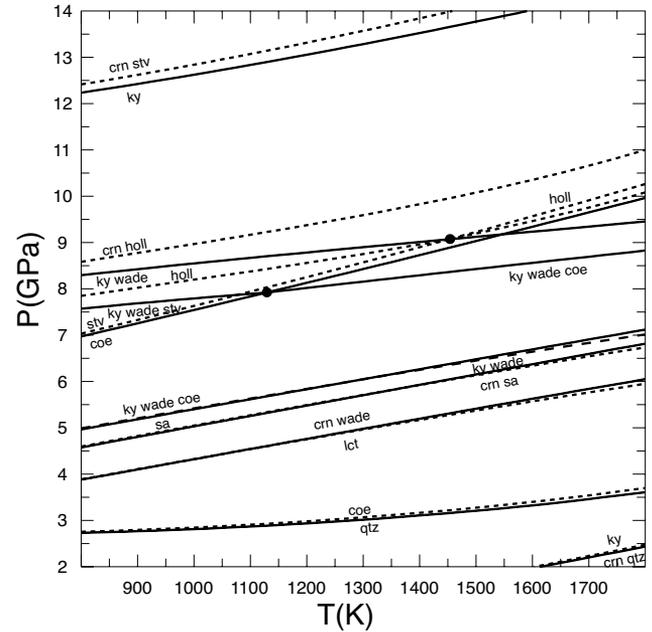


FIGURE 1. Plot of calculated stability fields for minerals in the $K_2O-Al_2O_3-SiO_2$ system using alternative equation of state formulations. Solid lines show stability fields calculated using the polythermal Murnaghan EOS (Eq. 6); dashed lines show them using the modified Murnaghan EOS. Notable differences occur in reactions involving wadeite, a phase that exhibits non-physical negative thermal expansivity due to the unmodified Murnaghan EOS. Most curves superimpose one another, indicating the equivalence of the two formulations at low pressures. Mineral name/abbreviations used: corundum/crn, stishovite/stv, coesite/coe, kyanite/ky, hollandite/holl, wadeite/wade, sanidine/sa, leucite/lct, quartz/qtz.

TABLE 1. Thermophysical data for selected phases

Name	V_r (J/bar)	$K_0 \times 10^{-5}$ /bar	$-dK/dT$ (bar/K)	$\alpha(T) = a_0 + a_1 T^{-1/2}$	
				$a_0 \times 10^5/K^{-1}$	$a_1 \times 10^4/K^{-1/2}$
leucite $KAlSi_3O_6$	8.828	6.58	94.5	3.67	3.67
sanidine $KAlSi_3O_8$	10.9	6.00	86.1	3.35	3.35
hollandite $KAlSi_3O_8$	7.128	18	237.6	3.3	0
wadeite $K_2Si_4O_9$	10.844	9	237.6	2.95	0
quartz SiO_2	2.2688	7.84	112.5	0.65	0.65
coesite SiO_2	2.064	10.45	150	1.8	1.8
stishovite SiO_2	1.4014	33.01	474	2.5	2.5
kyanite Al_2SiO_5	4.414	16.61	238.5	4.04	4.04
corundum Al_2O_3	2.558	26.33	378	4.19	4.19

Notes: $K' = 4$ for all phases. Source: Holland and Powell (1998) except for hollandite and wadeite (Yong et al. 2006).

1300 K is 8.1 GPa, the range of significant divergence shown in the figure. In the Holland and Powell (1998) database, we found that anomalies arise for pressures <10 GPa and temperatures <2000 K for about 10% of the end-member phases. Of interest is that all SiO_2 polymorphs, except stishovite, suffer from negative high-pressure thermal expansivity.

DISCUSSION

Simple to calculate equations of state are efficient for phase equilibrium calculations. We showed that two commonly used equations of state, the Murnaghan and the Birch-Murnaghan, are prone to non-physical behavior if their polythermal behavior is not properly parameterized. We focused on the positivity of thermal expansivity due to its role in defining the adiabatic gradient in planets ($dT/dz = \alpha g T / C_p$; g is gravitational acceleration and C_p is heat capacity) and its role in calculating seismic wavespeeds [e.g., $\rho V_p^2 = K_T(1 + T\alpha\gamma) + 4/3\mu$; γ is the Grüneisen parameter, ~ 1 for most substances, ρ the density, and μ is the shear modulus]. We showed how a straightforward change to the thermal component of the equation of state can remedy this flaw. The virtue is that at low pressures and temperatures, the calculated results using either parameterization are indistinguishable and the method advocated here does not lead to non-physical behavior under any circumstances. This is potentially of benefit in any phase equilibrium calculation implementation.

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REFERENCES CITED

- Anderson, O.L. and Isaak, D.G. (1993) The dependence of the Anderson-Grüneisen parameter δ_T upon compression at extreme conditions. *Journal of Physics and Chemistry of Solids*, 54, 221–227.
- Anderson, O.L., Isaak, D.G., and Oda, H. (1992) High-temperature elastic constant data on minerals relevant to geophysics. *Reviews of Geophysics*, 30, 57–90.
- Born, M. and Huang, K. (1954) *Dynamical Theory of Crystal Lattices*, xii+420 p. Clarendon, Oxford.
- Connolly, J.A.D. (2005) Computation of phase equilibria by linear programming: A tool for geodynamic modeling and its application to subduction zone decar-

- bonation. *Earth and Planetary Science Letters*, 236, 524–541.
- Connolly, J.A.D. and Kerrick, D.M. (2002) Metamorphic controls on seismic velocity of subducted oceanic crust at 100–250 km depth. *Earth and Planetary Science Letters*, 204, 61–74.
- Fei, Y.W. and Saxena, S.K. (1990) Internally consistent thermodynamic data and equilibrium phase relations for compounds in the system $MgO-SiO_2$ at high pressure and high temperature. *Journal of Geophysical Research*, 95, 6915–6928.
- Gerya, T.V., Podlesskii, K.K., Perchuk, L.L., and Maresch, W.V. (2004) Semiempirical Gibbs free energy formulations for minerals and fluids for use in thermodynamic databases of petrological interest. *Physics and Chemistry of Minerals*, 31, 429–455.
- Helffrich, G. and Kaneshima, S. (2004) Seismological constraints on core composition from Fe-O-S liquid immiscibility. *Science*, 306, 2239–2242.
- Holland, T.J.B. and Powell, R. (1998) An internally consistent thermodynamic data set for phases of petrological interest. *Journal of Metamorphic Geology*, 16, 309–343.
- Isaak, D.G., Carnes, J.D., Anderson, O.L., and Cynn, H. (1998) Elasticity of TiO_2 rutile to 1800 K. *Physics and Chemistry of Minerals*, 26, 31–43.
- Malvern, L.E. (1969) *Introduction to the Mechanics of a Continuous Medium*, xii+713 p. Prentice-Hall, Englewood Cliffs, New Jersey.
- Mattern, E., Matas, J., Ricard, Y., and Bass, J. (2005) Lower mantle composition and temperature from mineral physics and thermodynamic modelling. *Geophysical Journal International*, 160, 973–990.
- Poirier, J.-P. (1991) *An introduction to the physics of the Earth's interior*, x+264 p. Cambridge University Press, U.K.
- Pryde, A.K.A., Hammonds, K.D., Dove, M.T., Heine, V., Gale, J.D., and Warren, M.C. (1996) Origin of the negative thermal expansion in ZrW_2O_8 and ZrV_2O_7 . *Journal of Physics: Condensed Matter*, 8, 10973–10982.
- Richard, Y., Mattern, E., and Matas, J. (2005) Synthetic tomographic images of slabs from mineral physics. In R.D. van der Hilst, Ed., *Earth's Deep Mantle: Structure, Composition, and Evolution*, p. 285–302. AGU, Washington, D.C.
- Schumacher, J.C., Brady, J.B., Cheney, J.T., and Tonnsen, R.R. (2008) Glaucofan-bearing marbles on Syros, Greece. *Journal of Petrology*, 49, 1667–1686.
- Sobolev, S.V. and Babeyko, A.Y. (1994) Modeling of mineralogical composition, density, and elastic wave velocities in anhydrous magmatic rocks. *Surveys in Geophysics*, 15, 515–544.
- Stixrude, L. and Lithgow-Bertelloni, C. (2005) Mineralogy and elasticity of the oceanic upper mantle: Origin of the low-velocity zone. *Journal of Geophysical Research*, 110, B03204, DOI: 10.1029/2004JB002965.
- Yong, W., Dachs, E., Withers, A.C., and Essene, E.J. (2006) Heat capacity and phase equilibria of hollandite polymorph of $KAlSi_3O_8$. *Physics and Chemistry of Minerals*, 33, 167–177.

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