An Analytic Model of the Grüneisen Parameter at All Densities

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Abstract

We model the density dependence of the Grüneisen parameter as \( \gamma(\rho) = 1/2 + \gamma_1/\rho^{1/3} + \gamma_2/\rho^q \), where \( \gamma_1, \gamma_2, \) and \( q > 1 \) are constants. This form is based on the assumption that \( \gamma \) is an analytic function of \( V^{1/3} \), and was designed to accurately represent the experimentally determined low-pressure behavior of \( \gamma \). The numerical values of the constants are obtained for 20 elemental solids. Using the Lindemann criterion with our model for \( \gamma \), we calculate the melting curves for Al, Ar, Ni, Pd, and Pt and compare them to available experimental melt data. We also determine the \( Z \) (atomic number) dependence of \( \gamma_1 \). The high-compression limit of the model is shown to follow from a generalization of the Slater, Dugdale-MacDonald, and Vashchenko-Zubarev forms for the dependence of the Grüneisen parameter.

Key words: Grüneisen, Lindemann, density, melting, pressure, ultrahigh
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Introduction

Lattice anharmonicity leads to a volume dependence of the phonon frequencies, \( \omega_i \), that is described by the mode Grüneisen parameters [1]

\[
\gamma_i = \frac{\partial \ln \omega_i}{\partial \ln V}, \tag{1}
\]

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and the mechanical Grüneisen parameter is defined as the average of the $\gamma_i$ over the first Brillouin zone, $\gamma_m \equiv \langle \gamma_i \rangle$. When the $\gamma_i$ are all equal it can be shown \cite{2} that $\gamma_m = \gamma_i$ coincides with the thermodynamic Grüneisen parameter \cite{3}

$$\gamma_{th} = \frac{\alpha V B_T}{C_V},$$  \hspace{1cm} (2)

where $\alpha$ is the thermal expansion coefficient, $B_T$ is the isothermal bulk modulus, and $C_V$ is the heat capacity at constant volume. If the $\gamma_i$ are not all equal, $\gamma_m \neq \gamma_{th}$ in general. As noted by Barron \cite{3}, Born has shown that, even if the $\gamma_i$ are not all equal, $\gamma_m = \gamma_{th}$ in the limit of low ($T \to 0$) and high ($T \gtrsim \Theta_D$) temperatures. The $T = 0$ limiting value of $\gamma_m = \gamma_{th} \equiv \gamma = -d\ln \Theta_D/d\ln V$, where $\Theta_D$ is the Debye characteristic temperature, $\hbar\langle \omega_i^{-3}\rangle^{-1/3}/k_B$, in the limit $T \to 0$ \cite{3}. Here both $\Theta_D$ and $\gamma$ are functions of volume, or density, alone. This formula is the Debye-Grüneisen definition of $\gamma$ \cite{4}, which can be rewritten in terms of density, $\rho \sim 1/V$, as

$$\gamma(\rho) = \frac{d \ln \Theta_D(\rho)}{d \ln \rho}. \hspace{1cm} (3)$$

The Lindemann melting criterion, which asserts that the root-mean-square atomic displacement of atoms from their equilibrium positions in a solid is a fixed fraction of the interatomic distance at the melting point, can be rewritten in the form of the Gilvarry law, which relates the density derivative of the melting temperature, $T_m(\rho)$, to the Grüneisen parameter \cite{3}:

$$\frac{d \ln T_m(\rho)}{d \ln \rho} = 2 \left[ \gamma(\rho) - \frac{1}{3} \right],$$  \hspace{1cm} (4)

hence integration of $\gamma(\rho)$ yields the melt curve. Equations of state for solids can be constructed on the basis of $\gamma(\rho)$, though additional thermodynamic data are needed \cite{3}.

There is a long history of attempts to model $\gamma(\rho)$ \cite{10}. Slater \cite{8}, Dugdale and MacDonald \cite{9}, and Vashchenko and Zubarev \cite{10} proposed three expressions for $\gamma(\rho)$ that are summarized by the single formula \cite{11}:

$$\gamma = \frac{B' \rho - \frac{1}{6} - \frac{t}{3} \left( 1 - \frac{P}{3B} \right)}{1 - \frac{B'}{3B}},$$  \hspace{1cm} (5)

where $P$ is pressure on the cold curve ($T = 0$ equation of state), and $B \equiv -V dP/dV$ and $B' = (dP/dV)/(dP/dV)$ are the bulk modulus and its pressure derivative at $T = 0$. We will refer to Eq. (5) as the SDMVZ (Slater, Dugdale-MacDonald, Vashchenko-Zubarev) formula. Slater’s derivation is based on the Debye-Grüneisen definition (3) and assumes no volume dependence of the Poisson ratio. Dugdale and MacDonald used a simplification of lattice dynamics in which the material is modeled as a lattice undergoing one-dimensional harmonic oscillations. Their derivation was improved by Vashchenko and Zubarev who considered three-dimensional oscillations of a lattice with interatomic interactions described by an anharmonic central potential. Equation (5) reduces to the Slater, Dugdale-MacDonald, and Vaschenko-Zubarev formulas for $t = 0, 1, 2$, respectively. Eq. (5) has since been rederived by other researchers following different approaches \cite{12, 13, 14}. 

An analytic model for $\gamma(\rho)$

Melting curves and equations of state are usually based on simple functional forms for $\gamma(\rho)$. Dongquan and Wanxing [13], for example, proposed the form $\gamma(\rho) = \gamma_0\rho_0/\rho + 2/3 (1 - \rho_0/\rho)^\delta$, which reduces to $\gamma\rho \approx$ constant at small compressions and approaches $2/3$ as very large compressions; $\gamma$ does not differ from that given by Eq. (5) by more than 10% for $1 \leq \delta \leq 3$ [15]. For $\delta = 2$ this form reduces to $\gamma(\rho) = 2/3 + \gamma_1/\rho + \gamma_2/\rho^2$, a model frequently used for the construction of equations of state and melting curves [8, 16].

At very high compressions, of order 10, a solid becomes a crystallized one-component plasma, i.e., a lattice of ions in a uniform neutralizing background of electrons [17]. Several theoretical studies predict $\gamma = 1/2$ for this limiting state of a solid. Kopyshev [18] calculated $\gamma(V)$ in the Thomas-Fermi approximation and found $\gamma \to 1/2$ as $V \to 0$. Simple dimensional arguments by Hubbard [19] also indicate that $\gamma \to 1/2$ as $V \to 0$. Additional theoretical studies that give $\gamma \to 1/2$ include, but are not limited to, references [20, 21, 22, 23]. Nevertheless, some researchers assume $\gamma \to 2/3$ as $V \to 0$ [24] because that is the limiting value of $\gamma$ as given by Eq. (5) with fixed $t$ (see below).

We now construct a simple, practical three-parameter model of $\gamma(\rho)$ that accurately fits low-compression data, is equivalent to the experimental result that $\gamma \rho^{q_{\text{eff}}} \approx$ constant, $q_{\text{eff}} \geq 1$, for compressions up to 1.5, and limits to 1/2 as $V \to 0$. We assume that the Grüneisen parameter is an analytic function of $x \equiv V^{1/3}$, essentially the interatomic distance, and that the coefficient of $x$ in the Taylor-Maclaurin series expansion for $\gamma$ is non-zero. The simplest model that satisfies all of these requirements is

$$\gamma(V) = \frac{1}{2} + c_1 V^{1/3} + c_2 V^q, \quad c_1, c_2, q = \text{const}, \ q > 1,$$  \hspace{1cm} (6)

Note that $\gamma(V) - 1/2$ is asymptotic to $c_1 V^{1/3}$; this is discussed in more detail in the next section. The term $c_2 V^q$ represents the contribution of the quadratic and higher-order terms in $x$ which must sum to make $\gamma$ a concave-up function of $V$ at small compressions.

Eq. (6) can be rewritten in terms of density as

$$\gamma(\rho) = \frac{1}{2} + \frac{\gamma_1}{\rho^{1/3}} + \frac{\gamma_2}{\rho^q}, \quad \gamma_1, \gamma_2, q = \text{const}, \ q > 1,$$  \hspace{1cm} (7)

Note that both $\gamma_1$ and $\gamma_2$ are dimensional parameters.

Eq. (7) incorporates the low-compression power-law behavior $\gamma \rho^{q_{\text{eff}}} \approx$ constant, $q_{\text{eff}} \geq 1$, known from experiment. Experimental values of $q_{\text{eff}}$ are typically in the range 1 to 2 [25], but may be as high as 3 [26]. The effective exponent can be defined by $q_{\text{eff}} = -d \ln \gamma/d \ln \rho$ since $\gamma \sim \rho^{-q_{\text{eff}}}$; in our model we have $q_{\text{eff}} = [\gamma_1/(3 \rho^{1/3}) + q \gamma_2/\rho^q]/\gamma(\rho)$. Averaging over compressions from 1 to 1.25 we find $\langle q_{\text{eff}} \rangle \leq 3$ in general. Consider, for example, gold: with the corresponding parameters from Table 1, $q_{\text{eff}}$ varies from 4.7 at $\rho = 19.3$ g/cc to 1.3 at $\rho = 24$ g/cc with an average value of 2.7.

With $\gamma(\rho)$ given by Eq. (7), the Lindemann equation (4) can be integrated to yield the melting curve

$$T_m(\rho) = T_m(\rho_r) \left(\frac{\rho}{\rho_r}\right)^{1/3} \exp \left\{6 \gamma_1 \left(\frac{1}{(\rho_r)^{1/3}} - \frac{1}{\rho^{1/3}}\right) + \frac{2 \gamma_2}{q} \left(\frac{1}{(\rho_r)^q} - \frac{1}{\rho^q}\right)\right\},$$  \hspace{1cm} (8)

where $\rho_r$ and $T_m(\rho_r)$ are a reference density and corresponding melting temperature.
We now demonstrate that the asymptotic form of our model for the Gr"uneisen parameter follows from a generalization of the SDMVZ formula.

**Asymptotic $\gamma(\rho)$ from a generalization of the SDMVZ formula**

Parshukov [27] studied the compression dependence of $\gamma$ for lead, indium, and tin in the pressure range 0.6 to 4.0 GPa and found that it is almost identical for all three metals but is not described by Eq. (5) over the entire range of pressures for $t$ a constant. He found that the Slater formula ($t = 0$) provided the most accurate fit at small compressions while the Dugdale-MacDonald one ($t = 1$) is optimal at higher compressions. He suggested that all three ($t = 0, 1, 2$) formulas be unified by making $t$ compression dependent. Romain et al. [28] noted that the melting curve of Al cannot be described in the Lindemann approach using the $t = 0, 1, 2$ formulas for $\gamma(\rho)$. Nagayama and Mori [29] analyzed available experimental data on 16 metals and found that the data on $\gamma$ at $P = 0$ are best described by the Slater formula, but at moderate compressions the data are best fit by the Dugdale-MacDonald formula which is approximately equivalent to $\gamma/V^{1.1} = \text{constant}$, close to the relation $\gamma/V = \text{constant}$ that is routinely used in high-pressure studies. Nagayama and Mori noted that $d\ln \gamma/d\ln V$ decreases with increasing compression from the value given by the Slater formula ($t = 0$) through that given by the Dugdale-MacDonald formula ($t = 1$) toward the value predicted by the Vashchenko-Zubarev relation ($t = 2$). An analysis of Hugoniot data shows that $t$ follows a similar trend ($0 \to 1 \to 2$) in Al, Cu, and Ta [30]. These analyses of experimental data indicate that the parameter $t$ is not a constant but a variable that increases with increasing compression.

Irvine and Stacey [12] generalized the Vashchenko-Zubarev formula by accounting for non-central interatomic forces. They added a term $f$ to the expression for the interatomic force constant and obtained the formula

$$\gamma = \frac{B' - \frac{5}{6} + \frac{2P}{3B} - \frac{f}{18B} + \frac{1}{6} \frac{df}{dP}}{1 - \frac{4P}{3B} + \frac{f}{3B}},$$

which reduces to the Vashchenko-Zubarev formula for $f = 0$. By introducing the dimensionless parameter $t$ via

$$f = 2P(2 - t),$$

Eq. (9) reduces to

$$\gamma = \frac{B' - \frac{1}{6} - \frac{t}{3} \left(1 - \frac{P}{3B}\right) + \frac{P}{3B} V \frac{dt}{dV}}{1 - \frac{4tP}{3B}};$$

which would coincide with Eq. (5) without the additional term $(PV/3B) \frac{dt}{dV}$ in the numerator. Hence Eq. (11) is an extension of the SDMVZ formula, Eq. (5), to the case of density-dependent $t$. We note that Eq. (11) can be cast in the form

$$\gamma = \frac{1}{2} \frac{B}{B - \frac{2}{3} tP} \frac{d\left(B - \frac{2}{3} tP\right)}{dP} - \frac{1}{6} = -\frac{1}{2} \frac{d\ln \left(B - \frac{2}{3} tP\right)}{d\ln V} - \frac{1}{6},$$

(12)
which is equivalent to Eq. (5) if $t$ is a constant. In view of the experimental evidence that $t$ is a decreasing function of $V$ we use Eq. (11) rather than (5) for our subsequent analysis.

We consider Eq. (11) at ultrahigh pressures where the $(T = 0)$ equation of state is accurately given by \[P = aV^{-5/3}e^{-bV^{1/3}}, \quad a, b = \text{const} > 0.\] (13)

Eq. (13) includes an exponential screening correction to the equation of state of a free electron gas, namely \[P = aV^{-5/3}, \quad a = 2.337 \frac{Z^{5/3}}{\text{TPa}^{5}}, \quad Z \text{ being the atomic number}\] (22) It agrees with very accurate numerical Thomas-Fermi-Dirac results to within $2\%$ over the compression range of 1 to 15 with the exception of the alkali and alkaline-earth metals (31). Using the equation of state (13) in Eq. (11) we obtain

\[
\gamma = \frac{4(5 - 2t) + 2(4 - t) b \frac{V^{1/3}}{3} + b^2 \frac{V^{2/3}}{3} + 6 \frac{dt}{dV}}{6(5 - 2t + b \frac{V^{1/3}}{3})}.
\] (14)

It follows that $\gamma \rightarrow 2/3$ as $V \rightarrow 0$ for every asymptotic value of $t$ except $t = 5/2$. If $t = 5/2$ then $\gamma \rightarrow 1/2$ as $V \rightarrow 0$, in agreement with theoretical predictions. We conclude that $t$ is always asymptotic to $5/2$. Recent computer calculations of the compression dependence of $t$ for $\gamma$-Fe (3) corroborate this conclusion and also show that $t$ can saturate at quite moderate compressions: $t = 2.46 \pm 0.03$ at compressions of only 1.5 to 2.

The cold-curve $(T = 0)$ pressure (13) is an analytic function of $x$ everywhere except at the origin (infinite compression) where it has a pole of order five. (The majority of model equations of state are analytic in $x$ except for poles at $x = 0$. See Holzapfel (32) for a list of 16 examples.) Consequently, both $P/B$ and $B'$ are analytic for $x \geq 0$. Given the analyticity of $\gamma$, $P/B$, and $B'$ for $x \geq 0$, it follows from Eq. (11) that $t$ must also be an analytic function of $x$ for $x \geq 0$, hence it can be represented by the power series

\[
t = \frac{5}{2} - \sum_{i=1}^{\infty} t_i x^i.
\] (15)

The first sub-leading coefficient, $t_i$, must be non-negative if $t$ is in fact a monotonically increasing function of compression. Substituting this series in Eq. (14) and expanding we find that the asymptotic form of $\gamma$ is

\[
\gamma = \frac{1}{2} + \frac{b^2 + 2bt_1 - 2t_2}{6b + 12t_1} \frac{V^{1/3}}{3} + \ldots
\] (16)

It is expected that the $V^{1/3}$ term is always present in the series expansion of $\gamma$, i.e., $b^2 + 2bt_1 - 2t_2 \neq 0$. Thus the generalized SDMVZ formula leads to $\gamma \sim 1/2 + c_1 x$, $x \rightarrow 0$, in agreement with Eq. (6).

In summary, we have (i) generalized the SDMVZ formula for $\gamma(\rho)$ to account for a density-dependent $t$, (ii) shown that $\gamma$ goes to its theoretical high-pressure limit $1/2$ only if $t$ is asymptotic to $5/2$, and (iii) demonstrated that our model for the Grüneisen parameter and the generalized SDMVZ formula, Eq. (11), have the same asymptotic behavior provided $t$ is an analytic function of $x$, and $t(0) = 5/2$. 
Determination of model parameter values

In this section we outline the procedure for extracting the numerical values of the three model parameters \( \gamma_1, \gamma_2, \) and \( q \) from data and determine their values for 20 elemental solids.

Ideally, one would fit our model (7) to data on \( \gamma(\rho) \) and extract the values of \( \gamma_1, \gamma_2, \) and \( q \), but such data sets are very rarely available. Alternatively, one could fit the functional form (8) to \( T_m(\rho) \) data, but such data are very rarely available either since experiment usually determines \( T_m(P) \). Typically, the only available data on \( \gamma \) are \( \gamma(\rho_{300}) = \rho(P = 0, T = 300 \, ^\circ\text{K}) \), which is approximately equal to \( \gamma_m(T = 300 \, ^\circ\text{K}) \), and \( \gamma(\rho_m = \rho(P = 0, T = T_m)) \) which can be found by equating \( dT_m/d\rho \) at \( P = 0 \) as given by the Kraut-Kennedy law [33]

\[
T_m(\rho) = T_m(\rho_m) \left[ 1 + 2 \left( \gamma(\rho_m) - \frac{1}{3} \right) \left( \frac{\rho}{\rho_m} - 1 \right) \right]
\]

(17)
to \( dT_m/d\rho = (B_m/\rho_m) dT_m/dP \), where \( B_m \) and \( dT_m/dP \) at \( P = 0 \) are taken from experiment. The value of \( B_m \) is obtained by calculating bulk moduli at low temperatures from measured single-crystal elastic constants and then extrapolating to \( T_m \). The pressure derivative \( dT_m/dP \) is obtained either directly from low-pressure melting curve data or indirectly from isobaric-heating measurements of \( \Delta H (H \text{ is the enthalpy}) \) and \( \Delta V \) across the melting transition so that \( dT_m/dP = T_m \Delta V / \Delta H \) (Clau\-sius-Clapeyron equation). Eq. (17) is obtained by expanding \( T_m(\rho) \) in a power series about \( \rho_m \) using Eq. (4). Equation (7) with \( \rho = \rho_{300} \) and \( \rho = \rho_m \) provides two conditions needed to determine the three parameters \( \gamma_1, \gamma_2, \) and \( q \). The third condition comes from the ultrahigh pressure limit, which we discuss next.

The melting curve of a solid at ultrahigh pressures is described by the equation

\[
\frac{Z^2 e^2}{ak_B T_m} = \Gamma_m \tag{18}
\]

where \( a = (3v/4\pi)^{1/3} \) is the Wigner-Seitz radius (\( v \) being the Wigner-Seitz volume) and \( \Gamma_m \), a dimensionless constant, is the OCP coupling parameter at melt. The value of the coupling parameter is \( 170 - 180 \) for a body-centered cubic (bcc) OCP crystal [34] (the recent calculation of \( \Gamma_m \) for a bcc crystal by Potekhin and Chabrier [35] gave \( \Gamma_m = 175.0 \pm 0.4 \), and as high as \( 200 - 210 \) for a face-centered cubic (fcc) OCP crystal [36, 37]. In the following analysis we make no distinction between bcc and fcc OCP crystals and take \( \Gamma_m = 180 \).

It follows from Eq. (18), and Eq. (8) in the limit \( \rho \to \infty \) with \( \rho_r = \rho_m \) that

\[
T_m(\rho_m) v_m^{1/3} \exp \left\{ \frac{6\gamma_1}{\rho_m} + \frac{2\gamma_2}{q\rho_m} \right\} = \left( \frac{4\pi}{3} \right)^{1/3} \frac{e^2}{k_B} \frac{Z^2}{\Gamma_m},
\]

(19)

where \( v_m \), the Wigner-Seitz volume at the zero-pressure melting point, equals \( a_m^3/2 \) for a bcc and \( a_m^3/4 \) for a fcc crystal; \( a_m \) is the lattice constant.

We obtain the values of the parameters \( \gamma_1, \gamma_2 \) and \( q \) by simultaneous solution of three non-linear equations, namely Eq. (7) for \( \rho = \rho_{300} \) and \( \rho = \rho_m \), and Eq. (19) with \( \Gamma_m = 180 \). The value of \( \gamma(\rho_{300}) \), which is very rarely measured directly, can be approximated by
\(\gamma_{th}(300) = \alpha B_T/(\rho C_V)\) where \(\alpha\), \(B_T\), and \(C_V\) are all measured at 300 °K; the necessary room-temperature data can be found in ref. [38], and the data on \(\gamma_{th}(300)\) in ref. [39]. Parameter values for 20 elements are shown in Table 1; \(\gamma_1\) and \(\gamma_2\) are given to three significant figures, and \(q\) to two significant figures.

The uncertainty in the value of \(\gamma(\rho_m)\) is determined by the error bars on the measured melting temperatures and densities, usually a few percent (except perhaps for laser-heated diamond anvil cell (DAC) melt data, see below). Typical uncertainties in \(\alpha\), \(B_T\), and \(C_V\) result in an uncertainty of roughly 5% in the value of \(\gamma(\rho_{300})\) (we consider the difference between \(\gamma(\rho_{300})\) and \(\gamma_{th}(300)\) to be negligible). These uncertainties in \(\gamma(\rho_m)\) and \(\gamma(\rho_{300})\) imply an uncertainty \(\sim 5\%\) in \(\gamma_1\), values of \(q\) that are accurate to \(\sim 40\%\), and order-of-magnitude uncertainties in \(\gamma_2\) that are attributable to a very strong sensitivity to the value of \(q\). Let us take, as an example, copper; with \(\gamma(\rho_m) = 2.48\) and \(\gamma_{th}(300) = 2.19 \pm 0.1\) we find, neglecting uncertainties in the density, \(\gamma_1 = 1.84 \pm 0.08\), \(\gamma_2 = 430 - 1.95 \times 10^6\), and \(q = 4.7 \pm 2.0\).

Although the values of \(\gamma_2\) have order-of-magnitude uncertainties, we note that if Eq. (7) is rewritten in a “scaled” form, \(\gamma = 1/2 + \tilde{\gamma}_1(\rho_{300}/\rho)^{1/3} + \tilde{\gamma}_2(\rho_{300}/\rho)^q\), the values of both \(\tilde{\gamma}_1\) and \(\tilde{\gamma}_2\) are of order 1, as can be seen in Table 1 where we also include the values of both \(\tilde{\gamma}_1\) and \(\tilde{\gamma}_2\) to three significant figures.

| element | \(Z\) | \(\gamma_1\), \(\rho_{300}\) | \(\tilde{\gamma}_2\), \(\rho_{300}\) | \(q\) | \(\rho_{300}, g/cc\) | \(\rho_m, g/cc\) | \(T_m(\rho_m), ^\circ\text{K}\) |
|---------|------|-----------------|-----------------|-----|-----------------|-----------------|-----------------|
| Ne (fcc) | 10   | 1.04            | 5.17            | 0.91| 2.10            | 2.2             | 1.507            | 1.435           | 24.6            |
| Mg (hcp) | 12   | 0.79            | 4.33            | 0.66| 0.53            | 3.8             | 1.740            | 1.640           | 923             |
| Al (fcc) | 13   | 0.84            | 45.4            | 0.60| 1.40            | 3.5             | 2.700            | 2.550           | 933.5           |
| Ar (fcc) | 18   | 1.19            | 16.3            | 0.90| 1.86            | 3.8             | 1.771            | 1.622           | 83.8            |
| Fe (bcc) | 26   | 1.72            | 2.66 \times 10^3| 0.86| 0.25            | 4.5             | 7.870            | 7.270           | 1811            |
| Co (fcc) | 27   | 1.81            | 6.28 \times 10^4| 0.88| 0.39            | 5.5             | 8.830            | 8.180           | 1768            |
| Ni (fcc) | 28   | 1.85            | 5.60 \times 10^5| 0.89| 0.38            | 6.5             | 8.900            | 8.220           | 1728            |
| Cu (fcc) | 29   | 1.87            | 2.31 \times 10^4| 0.90| 0.78            | 4.7             | 8.930            | 8.370           | 1357.7          |
| Zn (hcp) | 30   | 1.91            | 1.84 \times 10^4| 0.99| 1.05            | 3.8             | 7.140            | 6.900           | 692.7           |
| Mo (bcc) | 42   | 2.06            | 1.40 \times 10^6| 0.95| 0.19            | 6.8             | 10.21            | 9.650           | 2896            |
| Pd (fcc) | 46   | 2.40            | 3.34 \times 10^6| 1.05| 0.25            | 6.6             | 12.02            | 11.29           | 1828            |
| Ag (fcc) | 47   | 2.23            | 9.63 \times 10^4| 1.02| 1.21            | 4.8             | 10.49            | 9.850           | 1235.1          |
| Cd (hcp) | 48   | 2.43            | 2.47 \times 10^4| 1.18| 0.97            | 4.7             | 8.650            | 8.420           | 594.2           |
| In (bct) | 49   | 2.43            | 6.14 \times 10^4| 1.25| 0.80            | 4.5             | 7.310            | 7.200           | 429.8           |
| Sn (bct) | 50   | 2.37            | 2.37 \times 10^4| 1.22| 0.83            | 4.0             | 7.300            | 7.200           | 505.1           |
| Pt (fcc) | 78   | 3.21            | 1.13 \times 10^{11}| 1.16| 1.01            | 8.3             | 21.45            | 20.19           | 2041            |
| Au (fcc) | 79   | 3.21            | 1.97 \times 10^{12}| 1.20| 1.62            | 9.4             | 19.30            | 18.29           | 1337.6          |
| Tl (bcc) | 81   | 3.17            | 3.74 \times 10^7| 1.39| 0.54            | 7.3             | 11.85            | 11.55           | 577             |
| Pb (fcc) | 82   | 3.09            | 8.21 \times 10^8| 1.38| 0.89            | 8.5             | 11.34            | 11.05           | 600.6           |
| U (bcc)  | 92   | 3.39            | 1.05 \times 10^{11}| 1.27| 0.57            | 8.8             | 19.05            | 17.60           | 1405            |

Table 1. Numerical values of the parameters entering Eqs. (7) and (8) for 20 elemental solids. The crystal structure indicated for an element is that from which it melts at zero pressure. For Ne and Ar the entry under \(\rho_{300}\) is the value of \(\rho(T = 0)\).

**Melting curves**

In this section we calculate melting curves using Eq. (8) with parameters determined in the previous section and compare the results with the available experimental data.
In Fig. 1 we compare our theoretical aluminum melting curve to experimental data [40]. Although the theoretical melting curve looks like a fit to the datapoints, the parameters $\gamma_1$, $\gamma_2$, and $q$ were not obtained from such a fit but rather from the zero-pressure data $\gamma(\rho_{300} = 2.7 \text{ g/cc}) = 2.5$ [39], $\gamma(\rho_m = 2.55 \text{ g/cc}) = 2.83$ [33], and $T_m(\rho_m) = 933.5 ^\circ \text{K}$, and Eqs. (7) and (19). In Figs. 2-4 we compare our theoretical melting curves for argon, nickel, palladium, and platinum to melting data available in the literature. Agreement between our theoretical curves and experiment is good with the exception of the lower-pressure data on nickel which were obtained from a laser-heated DAC [41]. This discrepancy may be due to systematic errors in the DAC data [42].

The $Z$ dependence of $\gamma_1$

It is evident from Table 1 that $\gamma_1$ is a slowly increasing function of atomic number. We have fit the forms $\gamma_1 = C_1 \cdot Z^n + C_2$ and $\gamma_1 = C_1 \cdot (\ln Z)^n + C_2$, where $C_1$, $C_2$ and $n$ are constants, to the table entries and find that the minimum $\chi^2$, 0.11, is realized for both $\gamma_1 = (12/11) Z^{1/3} - 11/7$ and $\gamma_1 = (2/21) (\ln Z)^{7/3} + 2/13$. These fits may be used to predict $\gamma_1$ in those cases where data provide only two constraints on $\gamma_1$, $\gamma_2$ and $q$. In Fig. 5 we plot $\gamma_1 = (2/21) (\ln Z)^{7/3} + 2/13$ along with the $\gamma_1(Z)$ entries in Table 1.

We note that the $\tilde{\gamma}_1$ entries in Table 1 can be fitted to the same functional form, i.e., $\tilde{\gamma}_1(Z) = (7/26) Z^{1/3} + 7/59$, but the accuracy of the fit is much lower than that of the $\gamma_1(Z)$ fit: $\chi^2 = 0.97$.

Concluding remarks

Our model for $\gamma$ accurately fits low-pressure data and agrees with theoretical predictions that $\gamma \to 1/2$ at ultrahigh pressures. Its accuracy cannot be determined at intermediate compressions because there are no experimental data. However, comparison of our calculated melting curves for aluminum and argon to the corresponding data in Figs. 1 and 2 demonstrates that our model is accurate up to compressions of at least 2. (Our calculated melting curve for copper, not discussed in this paper, is in excellent agreement with a new SESAME copper melting curve [3] up to compressions $\sim 10$.) In our model the deviation of $\gamma \rho^{\text{eff}}$ from a constant over the range of compressions from 1 to 1.5 is generally less than 10%. Finally, we note that our model for $\gamma$ can be used to calculate shear moduli along the solidus using Eq. (8) and the formula $G(\rho, T_m(\rho))/(\rho \cdot T_m(\rho)) = \text{constant}$ [43].

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Fig. 1

Fig. 2
**Figure captions**

Fig. 1. Melting curve of Al: Eq. (8) with the Al parameters from Table 1 vs. the experimental data [40] and the results of calculations [44] (larger points). The experimental points have error bars of $\sim 100 - 150$ °K which are not shown on the plot.

Fig. 2. Melting curve of Ar: Eq. (8) with the Ar parameters from Table 1 vs. the experimental data [45] and the results of calculations [46] (larger points).

Fig. 3. Melting curve of Ni: Eq. (8) with the Ni parameters from Table 1 vs. the experimental data [41]. The upper three points are shock-melting data from ref. [47] which does not quote error bars.

Fig. 4. Melting curves of Pd and Pt: Eq. (8) with the Pd and Pt parameters from Table 1 vs. shock-melting data [48] (upper two points of each curve, no error bars given) and zero-pressure datapoints (lowest points on each curve).

Fig. 5. Comparison of $\gamma_1 = (2/21) \ln Z^{7/3} + 2/13$ to the $\gamma_1(Z)$ entries in Table 1.
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\[ \gamma = \frac{t - 2}{3} - \frac{V}{2} \frac{d^2(PV^{2t/3})/dV^2}{d(PV^{2t/3})/dV}, \]

which is equivalent to (5) for constant \( t \).

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