Supporting Information

Thickness- and temperature-dependent Grüneisen parameter in thin films

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1. Theoretical Analysis

In thermodynamic treatment of a solid crystal with only the consideration of mechanical and thermal vibration (phonon) energies and without considering electron contributions, the Helmholtz free energy consists of two parts^[1-3], the potential free energy $F^{p,f}$ and the vibration free energy $F^{v,f}$ (or thermal energy), as given by

$$F^f = F^{p,f} + F^{\nu,f}.$$
 (S1)

If the potential free energy at temperature of absolute zero degree is used in the study of thermal properties of a system under constant volume, the potential free energy will be independent of temperature. The vibration free energy and internal energy at temperature T take the following form ^[4]:

$$F_T^{\nu,f} = \sum_{i,p} \left[\frac{1}{2} \hbar \omega_{i,p}^f + k_B T \ln \left(1 - e^{-\frac{\hbar \omega_{i,p}^f}{k_B T}} \right) \right],$$
(S2a)

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$$U_T^{\nu,f} = \sum_{i,p} \left[\frac{1}{2} \hbar \omega_{i,p}^f + \frac{\hbar \omega_{i,p}^f}{e^{\frac{\hbar \omega_{i,p}^f}{k_B T}} - 1} \right],$$
 (S2b)

respectively, where $\hbar = 1.05457 \times 10^{-34}$ J·s is the reduced Planck constant, $\omega_{i,p}^{f}$ is the angular frequency, *i* denotes the wavevector, *p* is the polarization index, and k_{B} is the Boltzmann constant.

Consider an ideal crystalline layer under biaxial in-plane deformation and without any shear and with the traction free condition along the layer plane normal direction. The biaxial strain is defined by $\varepsilon = \ln \frac{L}{L_0}$, where L_0 and L are the dimensions before and after the deformation, respectively. In general, the isothermal biaxial stress σ_T^f at temperature T in Lagrangian coordinates can be calculated from

$$2V\sigma_T^f = \left. \frac{\partial F^f}{\partial \varepsilon} \right|_T = \left. \frac{\partial F^{p,f}}{\partial \varepsilon} \right|_T + \left. \frac{\partial F^{\nu,f}}{\partial \varepsilon} \right|_T$$
(S3a)

where V is the volume of the studied film. We introduce Grüneisen parameters $\gamma^{\varepsilon_{xx}}$, $\gamma^{\varepsilon_{yy}}$, and $\gamma^{\varepsilon_{zz}}$ under normal strains ε_{xx} , ε_{yy} , and ε_{zz} , respectively, and the hydrostatic Grüneisen parameter $\gamma^e = \frac{1}{3}(\gamma^{\varepsilon_{xx}} + \gamma^{\varepsilon_{yy}} + \gamma^{\varepsilon_{zz}})$ under volumetric strain $e = \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}$ by following hydrostatic stress definition of $\sigma_h = \frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$, where σ_{xx} , σ_{yy} , and σ_{zz} are normal stresses. Under biaxial deformation, we have $\sigma_{zz} = 0$ and $\sigma_{xx} = \sigma_{yy} = \sigma^f$. Similarly, the Grüneisen parameter under biaxial deformation is $\gamma^f = \gamma^{\varepsilon_{xx}} = \gamma^{\varepsilon_{yy}}$ and $\frac{\partial \ln \omega_f^f}{\partial \varepsilon} \approx \frac{\partial \ln \omega f}{\partial \varepsilon} = \frac{\partial \ln \omega f}{\partial \ln L} = -\gamma^f$, where ω^f is the effectively averaged frequency under biaxial deformation. Thus, the explicit expression of Eq. (3a) is

$$2V\sigma_T^f = 2V\sigma_T^{p,f} - 2U_T^{\nu,f}\gamma^f \tag{S3b}$$

If no external stress is applied on the studied system, we shall have $\sigma_T^f = 0$ and

$$\hat{Y}^f V \varepsilon_T^{th,f} = U_T^{\nu,f} \gamma^f \tag{S3c}$$

where $\hat{Y}^{f} \varepsilon_{T}^{th,f} = \sigma_{T}^{p,f}$ and \hat{Y}^{f} is the biaxial modulus of the film. The strain $\varepsilon_{T}^{th,f}$ under the condition of $\sigma_{T}^{f} = 0$ is called the thermal biaxial strain. As discussed in the previous work ^[5], zero K is usually and inexplicitly taken as the reference temperature. When thermal expansion is considered, the studied system under stress-free condition will change its volume if temperature varies.

Following the Gibbs sharp surface approach, the thermal internal energy can be divided into the core and surface two parts, i.e.,

$$U_T^{\nu,f} = V u_T^{\nu,c} + 2A u_T^{\nu,s}, (S4a)$$

where $u_T^{\nu,c}$ and $u_T^{\nu,s}$ denote the thermal energy density per unit volume of the core and the thermal energy density per unit area of the surface, respectively, A is the surface area and the number of 2 is added here to represent two surfaces of the film. Eq. (S4a) can be rewritten as

$$U_T^{\nu,f} = V\left(u_T^{\nu,c} + \frac{2}{h}u_T^{\nu,s}\right) = Vu_T^{\nu,f},$$
 (S4b)

where *h* is the film thickness and $u_T^{\nu,f} = u_T^{\nu,c} + \frac{2}{h}u_T^{\nu,s}$ is the thermal energy density per unit volume of the film. Combining Eq. (S4b) with Eq. (S3c) gives

$$\hat{Y}^{f}\varepsilon_{T}^{th,f} = \left(u_{T}^{\nu,c} + \frac{2}{h}u_{T}^{\nu,s}\right)\gamma^{f}.$$
(S4c)

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Partially differentiating Eq. (S4c) with respect to temperature under constant volume yields

$$\frac{\partial \hat{Y}^{f}}{\partial T}|_{V}\varepsilon_{T}^{th,f} + \hat{Y}^{f}\alpha_{T}^{f} = \left(c_{T}^{c} + \frac{2}{h}c_{T}^{s}\right)\gamma^{f} + \left(u_{T}^{\nu,c} + \frac{2}{h}u_{T}^{\nu,s}\right)\frac{\partial\gamma^{f}}{\partial T}|_{V},$$
(S4d)

where α_T^f is the Thermal Expansion Coefficient (TEC) of the film, $c_T^c = \frac{\partial u_T^{v,c}}{\partial T}|_V$ and $c_T^s = \frac{\partial u_T^{v,s}}{\partial T}|_V$ are the heat capacity density per unit volume of the core and the heat capacity density per unit area of the surface, respectively. From the analysis, we have the heat capacity density per unit volume of the film

$$c_T^f = c_T^c + \frac{2}{h}c_T^s. \tag{S4e}$$

As described in the previous works ^[19-28], when the stress-free bulk counterpart is taken as the reference, the in-plane dimension of a thin film will be deformed and the initial deformation is caused by isothermal relaxation without any external loads, which changes the film in-plane length and the length change depends on the film thickness. Thus, the equilibrium length called the initial length L_T^{ini} of a film at temperature T is given by

$$L_T^{\rm ini} = L_T^0 \exp(\varepsilon_T^{\rm ini}), \tag{S5a}$$

with L_T^0 being the length before relaxation as that in the stress-free bulk counterpart and $\varepsilon_T^{\text{ini}}$ is the initial strain, which is expressed by

$$\varepsilon_T^{\text{ini}} = -\frac{2\sigma_{0,T}^s}{h\hat{Y}_T^c + 2\hat{Y}_T^s},\tag{S5b}$$

where $\sigma_{0,T}^{s}$ is the surface eigenstress at temperature *T*, \hat{Y}_{T}^{c} and \hat{Y}_{T}^{s} are the core and surface biaxial moduli, respectively.

If the thermodynamic properties of a studied sample at temperature T_0 are taken as the reference, we are able to calculate the change in the thermodynamic properties induced by temperature change $\Delta T = T - T_0$. When the temperature varies from T_0 to T, the thermal strains of the film and the core are given respectively by

$$\varepsilon_{T_0 \to T}^f = \ln\left(\frac{L_T^{\text{ini}}}{L_{T_0}^{\text{ini}}}\right) = \int_{T_0}^T \alpha_T^f \,\mathrm{dT}\,,\tag{S5c}$$

$$\varepsilon_{T_0 \to T}^c = \ln\left(\frac{L_T^0}{L_{T_0}^0}\right) = \int_{T_0}^T \alpha_T^c \mathrm{dT} \,. \tag{S5d}$$

Based on the Varshni equation ^[6], Zhou et al.^[7] proposed a linearly temperature-dependent biaxial Young's modulus when temperature is higher than 100 K, which is given by

$$\hat{Y}_{T}^{f} = \hat{Y}_{T_{0}}^{c} + 2\frac{\hat{Y}_{T_{0}}^{s}}{h} - \left(k^{c} + 2\frac{k^{s}}{h}\right)\Delta T,$$
(S6a)

where the superscripts "f", "c", and "s" denote "film", "core", and "surface", respectively, and k is the thermal coefficient of biaxial Young's modulus. The same simplification scheme^[7] leads to the size-dependent TEC of the film

$$\alpha^{f} = \frac{\alpha^{c} - \frac{2k^{s}}{hk^{c}}\alpha^{s}}{1 + \frac{2k^{s}}{hk^{c}}}.$$
(S6b)

Substituting Eq. (S6a) into Eq. (S4d) leads to

$$\begin{split} & \left[\hat{Y}_{T_0}^c + 2\frac{\hat{Y}_{T_0}^s}{h} - \left(k^c + 2\frac{k^s}{h}\right)\Delta T\right]\alpha^f \\ &= \left(c_T^c + \frac{2}{h}c_T^s\right)\gamma^f + \left(u_{T_0 \to T}^{\nu,c} + \frac{2}{h}u_{T_0 \to T}^{\nu,s}\right)\frac{\partial\gamma^f}{\partial T}|_V, \end{split}$$
(S6c)

We may further assume that the heat capacity densities of c_T^c and c_T^s be constants, which is available when the temperature is above the Debye temperature of a metal in study, and then simplify Eq. (S6c) to

$$\left[\hat{Y}_{T_0}^c + 2\frac{\hat{Y}_{T_0}^s}{h} - 2\left(k^c + 2\frac{k^s}{h}\right)\Delta T\right]\alpha^f = \left(c^c + \frac{2}{h}c^s\right)\gamma^f + \left(c^c + \frac{2}{h}c^s\right)\Delta T\frac{\partial\gamma^f}{\partial T}|_V.$$
 (S6d)

Eq. (S6d) indicates that the film Grüneisen parameter is a linear function of ΔT ,

$$\gamma^f = \gamma_0^f + \gamma_1^f \Delta T, \qquad (S7a)$$

With Eq. (S7a), Eq. (S6d) is rewritten as

$$\left[\hat{Y}_{T_0}^c + 2\frac{\hat{Y}_{T_0}^s}{h} - 2\left(k^c + 2\frac{k^s}{h}\right)\Delta T\right]\alpha^f = \left(c^c + \frac{2}{h}c^s\right)\left(\gamma_0^f + \gamma_1^f\Delta T\right) + \left(c^c + \frac{2}{h}c^s\right)\Delta T\gamma_1^f, (S7b)$$

Eq. (S7b) yields

$$\gamma_{0}^{f} = \frac{\left(\hat{Y}_{T_{0}}^{c} + 2\frac{\hat{Y}_{T_{0}}^{s}}{h}\right)\alpha^{f}}{\left(c^{c} + \frac{2}{h}c^{s}\right)},$$
(S7c)

$$\gamma_1^f = -\frac{\left(k^c + 2\frac{k^s}{h}\right)\alpha^f}{\left(c^c + \frac{2}{h}c^s\right)}.$$
(S7d)

Eqs. (S7a, c, d) are corresponding to Eqs. (1a-c) in the main text, respectively. Eqs. (S7c, d) show that both γ_0^f and γ_1^f depend on the film thickness, thereby the Grüneisen parameter of

a film is thickness- and temperature-dependent. For sufficiently thick films, $\hat{Y}_{T_0}^c \gg 2 \frac{\hat{Y}_{T_0}^s}{h}$, $c^c \gg \frac{2}{h}c^s$, $k^c \gg 2 \frac{k^s}{h}$, and $\alpha^f \to \alpha^c$, the thickness-dependence will disappear.

In the above analysis, we assume the heat capacity densities of the core and surface be constant and independent of temperature. If the change of volume with temperature is considered, the heat capacity densities of the core and surface will change with temperature. The film volume V_T at temperature T is expressed with the thermal expansion coefficient α^f as

$$V_T = V_{T_0} (1 + 3\alpha^f \Delta T), \tag{S8a}$$

where V_{T_0} is the volume at temperature T_0 . In statistic physics, the core thermal internal energy is described by the product of atom number *N* of the core and the thermal internal energy per atom, $\hat{u}^{\nu,c}$. Similarly, the surface energy can be estimated by the product of the gained energy per broken bond, $\hat{u}^{\nu,s}$, times the number *M* of broken bonds in one surface. Then, the thermal internal energy of a film is given by

$$U_{T}^{\nu,f} = N\hat{u}^{\nu,c} + 2M\hat{u}^{\nu,s}.$$
 (S8b)

Consequently, the thermal capacity under constant volume of the film, C^{f} , is calculated to be

$$C^f = N\hat{c}^c + 2M\hat{c}^s, \tag{S8c}$$

where \hat{c}^c is the thermal capacity under constant volume per atom and \hat{c}^s is the heat capacity under constant volume per broken bond. In the following analysis, we assume both \hat{c}^c and \hat{c}^c be constants, independent of temperature and then rewrite Eq. (S6c) as

$$\left[\hat{Y}_{T_0}^c + 2\frac{\hat{Y}_{T_0}^s}{h} - 2\left(k^c + 2\frac{k^s}{h}\right)\Delta T\right](1 + 3\alpha^f \Delta T)\alpha^f$$
$$= \left(\frac{N}{V_{T_0}}\hat{c}^c + 2\frac{M}{V_{T_0}}\hat{c}^s\right)\gamma^f + \left(\frac{N}{V_{T_0}}\hat{c}^c + 2\frac{M}{V_{T_0}}\hat{c}^s\right)\Delta T \left.\frac{\partial\gamma^f}{\partial T}\right]_V.$$
(S8d)

The term $\frac{N}{V_{T_0}}\hat{c}^c$ is actually the heat capacity density per unit volume at temperature T_0 , $c_{T_0}^c$. In analogy, we introduce the heat capacity density per unit surface area at temperature T_0 , $c_{T_0}^s$. With $c_{T_0}^c$ and $c_{T_0}^s$, Eq. (S8d) is rewritten as

$$\left[\hat{Y}_{T_{0}}^{c} + 2\frac{\hat{Y}_{T_{0}}^{s}}{h} - 2\left(k^{c} + 2\frac{k^{s}}{h}\right)\Delta T\right](1 + 3\alpha^{f}\Delta T)\alpha^{f}$$
$$= \left(c_{T_{0}}^{c} + \frac{2}{h_{T_{0}}}c_{T_{0}}^{s}\right)\gamma^{f} + \left(c_{T_{0}}^{c} + \frac{2}{h_{T_{0}}}c_{T_{0}}^{s}\right)\Delta T\left.\frac{\partial\gamma^{f}}{\partial T}\right]_{V},$$
(S9a)

Eq. (S9a) requires that γ^f takes the form of

$$\gamma^f = \gamma_0^f + \gamma_1^f \Delta T + \gamma_2^f (\Delta T)^2, \tag{S9b}$$

Combining Eq. (S9b) and Eq. (S9a) gives

$$\alpha^{f} \left\{ \hat{Y}_{T_{0}}^{c} + 2\frac{\hat{Y}_{T_{0}}^{s}}{h} + \left[3\alpha^{f} \left(\hat{Y}_{T_{0}}^{c} + 2\frac{\hat{Y}_{T_{0}}^{s}}{h} \right) - 2\left(k^{c} + 2\frac{k^{s}}{h}\right) \right] \Delta T - 6\alpha^{f} \left(k^{c} + 2\frac{k^{s}}{h}\right) (\Delta T)^{2} \right\}$$

$$= \left(c_{T_{0}}^{c} + \frac{2}{h_{T_{0}}} c_{T_{0}}^{s} \right) \gamma_{0}^{f} + 2\left(c_{T_{0}}^{c} + \frac{2}{h_{T_{0}}} c_{T_{0}}^{s} \right) \gamma_{1}^{f} \Delta T + 3\left(c_{T_{0}}^{c} + \frac{2}{h_{T_{0}}} c_{T_{0}}^{s} \right) \gamma_{2}^{f} (\Delta T)^{2}.$$
(S9c)

Eq. (S9c) yields

$$\left(c_{T_0}^c + \frac{2}{h_{T_0}}c_{T_0}^s\right)\gamma_0^f = \alpha^f \left(\hat{Y}_{T_0}^c + 2\frac{\hat{Y}_{T_0}^s}{h}\right),$$
 (S10a)

$$2\left(c_{T_{0}}^{c} + \frac{2}{h_{T_{0}}}c_{T_{0}}^{s}\right)\gamma_{1}^{f} = \alpha^{f}\left[3\alpha^{f}\left(\hat{Y}_{T_{0}}^{c} + 2\frac{\hat{Y}_{T_{0}}^{s}}{h}\right) - 2\left(k^{c} + 2\frac{k^{s}}{h}\right)\right],$$
 (S10b)

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$$\left(c_{T_0}^c + \frac{2}{h_{T_0}}c_{T_0}^s\right)\gamma_2^f = -2(\alpha^f)^2\left(k^c + 2\frac{k^s}{h}\right).$$
 (S10c)

Eqs. (S9b, S10a-c) are corresponding to Eqs. (2a-d) in the main text, respectively. Eqs. (S10a, b, c) indicate again that all γ_0^f , γ_1^f , and γ_2^f depend on the film thickness. In brevity, the theoretical analysis gives the explicit equations of the thickness- and temperature-dependent Grüneisen parameter and Grüneisen equation. The difference between the two theoretical analyzes is how to approximately treat the core heat capacity density per unit volume and the surface heat capacity density per unit surface area. In the temperature linear dependence of the Grüneisen parameter, the values of core and surface heat capacity densities are taken at highest temperature T_0 , or a temperature between them in the temperature range of interest, while in the temperature quadratic dependence of the Grüneisen parameter, the values of core and surface heat capacity T_0 .

2. Calculation results and curve fitting



Figure S1: Thermal strain (a), biaxial Young's modulus (b) of FCC Ni, Cu, and Au bulk crystals versus temperature. Points are simulation results, and the solid lines denote the perfect linear fittings with the analysis.

Fig. S1(a) shows the thermal strain versus temperature, indicating that the Thermal Expansion Coefficient (TEC) of the bulk Ni, Cu, Au with temperature increasing, and the slopes denote the thermal expansion coefficients of the bulk crystal. Fig. S1(b) shows the bulk biaxial Young's modulus decrease linearly with temperature increasing. The slopes between the bulk biaxial Young's modulus and temperature give the value of the thermal coefficient of the bulk biaxial Young's modulus k^c , as listed in table 1.



Figure S2: Initial strain of thin films versus temperature and thickness, where the solid lines in (a,c,e) are linear fittings of Eq. (S5a), and the curves in(b, d, f) are fittings of Eq. (S5b).

Fig. S2(a, c and e) show the initial strains versus temperature, where the solid lines represent the perfect linear fitting of the results, meaning the independence between the Thermal Expansion Coefficient (TEC) α^{f} and temperature for a given thickness film. Fig. S2(b, d and f) show the initial strain versus thickness for a given temperature. Fitting the simulation results with Eq. (S5b) gives the surface eigenstresses and surface biaxial Young's modulus of the films at each of the simulated temperatures.



Figure S3: Surface biaxial Young's modulus, fitted out by using Eq. (S5b), as a function of temperature.

Fig. S3 shows the surface biaxial Young's moduli of the films versus temperature, which also decreases linearly with increasing temperature, similar to the bulk biaxial Young's modulus. The slopes between surface biaxial Young's modulus and temperature give the value of the thermal coefficient of the surface biaxial Young's modulus k^s , as listed in Table 2-4.



Figure S4: The nominal biaxial Young's moduli of thin films versus temperature and thickness, defined as $\hat{Y}^f = \hat{Y}^c + \frac{2}{h}\hat{Y}^s$.

Fig. S4(a,c,e) show the film nominal biaxial Young's moduli \hat{Y}^f decrease linearly with temperature increasing for a given thickness film, which is similar to \hat{Y}^c and \hat{Y}^s , and consistent with the simplified Varshni equation. Fig. S4(b,d,f) show the film nominal biaxial Young's moduli \hat{Y}^f are also dependent on thickness. For a given temperature, the nominal biaxial Young's moduli \hat{Y}^f decrease with thickness increasing, and the rate of decreasing slows down gradually. With thickness increasing, nominal biaxial Young's moduli \hat{Y}^f will approach the bulk biaxial Young's moduli \hat{Y}^c gradually, which is because the effect of the surface will reduce with increasing thickness, consistent to the thermo-mechanical properties in thin films.



Figure S5: The dimensionless film TEC α^f/α^c versus thickness.

The dimensionless film TEC α^f / α^c is the ratio of the Thermal Expansion Coefficient (TEC) of the film and of the bulk counterpart. Fig. S5 shows the dimensionless film TEC α^f / α^c versus thickness. The dimensionless TEC approaches one with the thickness increasing, meaning that TEC of the film will approach the corresponding bulk value when the film thickness is sufficiently large, which agrees to Eq. (S6b).

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