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Microscopics of the thermoelastic effect

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Abstract

The micromechanism of the thermoelastic effect (changes in temperature of a solid on its adiabatic elastic loading) is treated using the model of a loaded anharmonic oscillator. Loading leads to changes in frequency and, hence, to changes in the oscillation energy of the oscillators, thereby changing the temperature of a solid. The complicated energetics of loading of an excited anharmonic oscillator associated with conversion of the oscillation energy into static potential energy, and the reverse process, is described. Relevant problems are discussed.

Keywords: Mechanism; Model; Thermoelastic

1. Introduction

The thermoelastic effect is a change in temperature of a solid on its adiabatic loading leading to elastic deformation of the solid (compression or extension).

The thermodynamic derivation of the expression for temperature changes of a solid (ΔT) on its adiabatic elastic deformation by a stress σ at temperature T, yields in the first approximation [1]

$$\frac{\Delta T}{T} = -\frac{\alpha}{C}\sigma \tag{1}$$

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where α is the coefficient of linear (uniaxial) thermal expansion and C is the specific heat capacity (per unit volume).

Eq. (1) describes fairly well the experimental data for elastic low-molecular solids [1,2].

The thermodynamic analysis shows that the thermoelastic effect and thermal expansion of a solid are correlated, but it does not reveal the microscopic mechanism of this effect.

This paper considers the thermoelastic effect and discusses relevant problems.

2. Loading of an anharmonic oscillator

It is well known that, from the point of view of oscillation dynamics, a solid can be represented as a set of anharmonic oscillators [3]. Therefore, it is reasonable to see how loading affects the behaviour of a basic element of the dynamics of a solid, i.e. an anharmonic oscillator.

The potential well for a one-dimensional anharmonic oscillator has the shape shown in Fig. 1 and in the region of small oscillation amplitudes is approximately described by

$$U(r) \approx -D + \tfrac{1}{2}f(r-r_0)^2 - \tfrac{1}{3}g(r-r_0)^3 \qquad (2)$$

where D is the well depth (dissociation energy), f is the coefficient of linear elasticity, g is the coefficient of non-linear elasticity (anharmonicity), and r_0 is the coordinate of the well bottom.

The adiabatic application (fairly slow and quasi-equilibrium) of force F along the oscillator axis displaces the well bottom by

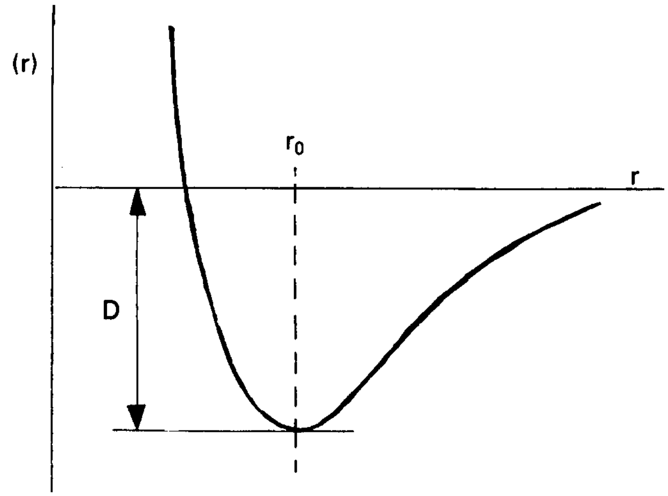

Fig. 1. Potential well at anharmonic interaction.

$$\Delta r = \frac{f}{2g}\left(1 - \sqrt{1 - \frac{4g}{f^2}F}\right)$$

In this case the well shape, i.e. its curvature near the bottom, also changes. Therefore, the coefficient of linear elasticity also changes

$$f_F = f\left(1 - \frac{2g}{f}\Delta r\right) = f\sqrt{1 - \frac{4g}{f^2}F} \simeq f\left(1 - \frac{2g}{f^2}F\right) \tag{3}$$

This approximation is valid for small F (compared with the maximum elastic force $F_m = f^2/4g$ in the potential (2)).

In contrast to the harmonic oscillator, the oscillation frequency of an anharmonic oscillator (2) depends on the degree of its excitation (on energy E_{osc} or oscillation amplitude). Approximately [4]

$$\nu = \frac{1}{2\pi}\sqrt{\frac{f}{mq(E_{osc})}} \tag{4}$$

where m is the mass of the oscillator, and $q(E_{osc})$ is the oscillation-energy-dependent coefficient. At low energies (E_{osc} is much less than D), $q(E_{osc})$ is slightly higher than unity [4].

Then, if the oscillation frequency of an unloaded oscillator is ν, the frequency of a loaded anharmonic oscillator will be

$$\nu_F = \frac{1}{2\pi}\sqrt{\frac{f_F}{mq(E_{osc})}} \tag{5}$$

If force F is positive, i.e. it is directed towards increasing r (bond extension in the oscillator), the frequency decreases. If F is negative (bond compression), the frequency increases.

It is known [5] that the adiabatic invariant for the oscillator is the ratio between its oscillation energy and frequency

$$\frac{E_{osc}}{\nu} = \text{const} \tag{6}$$

In other words, in the case of a slow (adiabatic) variation of the oscillator parameters its oscillation energy changes proportionally to the frequency variations.

It follows from Eq. (6) that

$$\frac{\Delta E_{osc}}{E_{osc}} = \frac{\Delta\nu}{\nu} \tag{7}$$

where ΔE_{osc} and $\Delta\nu$ are interrelated changes of E_{osc} and ν (generally speaking, they are small). When the oscillator is loaded, we obtain from Eq. (5)

$$\Delta\nu = \nu_F - \nu = -\nu\frac{g}{f^2}F$$

and then

$$\frac{\Delta E_{\mathrm{osc}}}{E_{\mathrm{osc}}} \simeq -\frac{g}{f^2} F \tag{8}$$

In the simplest classical model of a solid as a system consisting of similar atom-oscillators, the average oscillation energy per degree of freedom at temperature T is

$$\bar{E}_{\mathrm{osc}} = KT$$

where K is the Boltzmann constant. Hence

$$\frac{\Delta \bar{E}_{\mathrm{osc}}}{\bar{E}_{\mathrm{osc}}} = \frac{\Delta T}{T}$$

Then, taking into account Eq. (8), we obtain

$$\frac{\Delta T}{T} = -\frac{g}{f^2} F \tag{9}$$

Thus, we have derived an expression for the changes in temperature of a solid on its loading (the thermoelastic effect) caused by changes in the oscillation energy of the anharmonic oscillators being loaded.

It is also easy (or even easier) to derive the expression for the thermoelastic effect when the anharmonic oscillators are quantum oscillators, i.e. they have a discrete set of oscillation energy levels.

The population of any energy level E_n is proportional to the Boltzmann factor $\exp(-E_n/KT)$. The population of levels remains unaltered on adiabatic loading [6] and, hence, here $E_n/T = \mathrm{const.}$

In the quantum case $E_n = h\nu(0.5 + n)$, where n is the quantum number, which is not an integer for an anharmonic oscillator, in contrast to the harmonic oscillator [4]. This expression for E_n can be regarded as the quantum consequence of the adiabatic invariance (see Eq. (6)) at $n = \mathrm{const.}$

As a result, we obtain $\nu/T = \mathrm{const.}$ From this, using Eq. (5), we come again to Eq. (9), i.e. to the description of the thermoelastic effect.

We will show that Eq. (9) is identical to the thermodynamic expression (1). The coefficient of thermal expansion is $\alpha = \mathrm{d}\bar{\varepsilon}(T)/\mathrm{d}T \simeq (g/f^2 r_0)/(\mathrm{d}\bar{E}_{\mathrm{osc}}/\mathrm{d}T)$ (see Eq. (13)). The specific heat capacity is $C \approx (1/r_0^3)/(\mathrm{d}\bar{E}_{\mathrm{osc}}/\mathrm{d}T)$ (because the quantity of atom-oscillators in a unit volume is approx. r_0^{-3}). Stress is $\sigma \approx F/r_0^2$ (because r_0^2 is approx. the cross section of the atom oscillator).

Then $\Delta T/T = -(\alpha/C)\sigma \approx -(g/f^2)F$, i.e. it coincides with Eq. (9).

Therefore, the physical mechanism of the thermoelastic effect is the change in the oscillation frequency of loaded anharmonic oscillators. This gives rise to changes in the oscillation energy of oscillators, and, as a consequence, to variations in the temperature of a solid, which is an ensemble of these oscillators from the dynamic point of view.

3. Specific features of the energetics of the thermoelastic effect

Let us consider the energy aspects of the loading of an anharmonic oscillator.

From Eq. (2), the adiabatic deformation of an elastic bond Δr by force F leads to a change in the static potential energy ΔU, i.e. a change in the energy associated with the displacement of the well bottom, given by

$$\Delta U = \tfrac{1}{2}f(\Delta r)^2 - \tfrac{1}{3}g(\Delta r)^3 \approx \tfrac{1}{2}fr_0^2\varepsilon^2 - \tfrac{1}{3}gr_0^3\varepsilon^3 \approx \tfrac{1}{2}fr_0^2\varepsilon^2 \tag{10}$$

where $\Delta r/r_0 = \varepsilon$ is a relative bond deformation, and at small ε ($\varepsilon \ll 1$), the term of the third order with respect to ε can be neglected.

For a harmonic oscillator, the energy problems would be closed by such a change in the static component of potential energy on loading.

For the anharmonic oscillator, the situation is different. As Eq. (8) shows, the adiabatic loading gives rise not only to changes in the static potential energy, but also to changes in the oscillation energy.

In the approximation of the first order with respect to ε

$$F \approx fr_0\varepsilon$$

Then, from Eq. (8)

$$\Delta E_{\text{osc}} \simeq -E_{\text{osc}}\frac{g}{f}r_0\varepsilon \tag{11}$$

Note that $(g/f)r_0 = \gamma$ corresponds to Gruneissen's coefficient.

The total energy variation of the oscillator will be

$$\Delta W(\varepsilon) = \Delta E_{\text{osc}}(\varepsilon) + \Delta U(\varepsilon) \simeq -E_{\text{osc}}\frac{g}{f}r_0\varepsilon + \tfrac{1}{2}fr_0^2\varepsilon^2 \tag{12}$$

The $\Delta E_{\text{osc}}(\varepsilon)$, $\Delta U(\varepsilon)$ and $\Delta W(\varepsilon)$ dependences are shown in Fig. 2.

The situation is highly surprising. At low degrees of extension, the total oscillator energy decreases. The paradox is that the external force (F), no doubt, does work extending the bonds in the oscillator, but the total oscillator energy reduces. This change in the total energy is evidently due to the different effects of variations in U and E_{osc} in the region of positive ε, ΔU being quadratic with respect to ε and ΔE_{osc} being linear (quasi-linear). The situation becomes understandable if we take into account the initial dynamic (both zero and thermal) expansion (ε_0) of the excited anharmonic oscillator.

The value of ε_0 can be estimated from the condition of the minimum of the total oscillator energy which is equivalent to

$$\frac{\mathrm{d}[\Delta W(\varepsilon)]}{\mathrm{d}\varepsilon} = 0$$

Then we obtain

$$\varepsilon_0 = E_{\text{osc}}\frac{g}{f^2r_0} \tag{13}$$

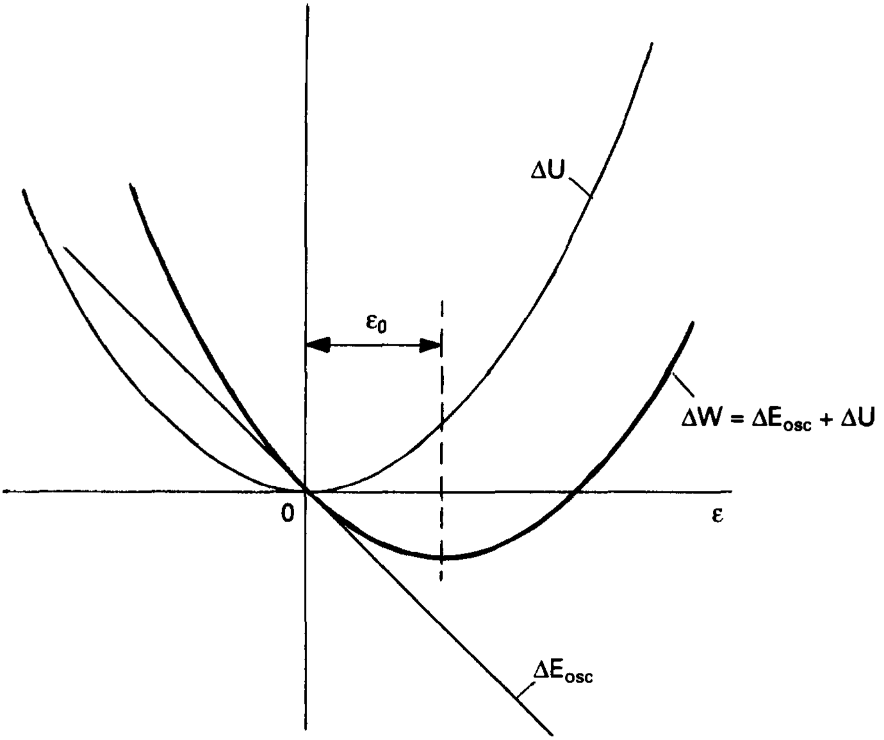

Fig. 2. Changes of different energy components on adiabatic loading (deformation) of an anharmonic oscillator: ε, relative extension (compression) of an elastic bond in the oscillator; ΔU, change in the static component of the potential energy; ΔE_{osc}, change in the oscillation energy of the oscillator; $\Delta W = \Delta E_{\mathrm{osc}} + \Delta U$, change in the total oscillator energy.

The value of ε_0 corresponds to the position of the minimum of the $\Delta W(\varepsilon)$ dependence in Fig. 2.

In this case, both extension and compression counted off from ε_0 give rise to an increase of the total oscillator energy that occurs at the expense of the work done by the external force.

The detailed energetics of an adiabatically loaded anharmonic oscillator are complex.

As the oscillator is compressed from $\varepsilon = \varepsilon_0$ to $\varepsilon = 0$, the static potential energy decreases (Fig. 2). Apparently this energy change, together with the work done by the external force, contributes to a growth in the oscillation energy, i.e. the static potential energy is converted into the oscillation energy. On further compression (from $\varepsilon = 0$ to small values of $-\varepsilon$), almost all the work done by the external force is spent on the oscillation energy growth.

The reverse process occurs on oscillator extension from $\varepsilon = \varepsilon_0$. A decrease in the oscillation energy leads to an additional growth in the static potential energy (additional with respect to the work of the external force), i.e. the oscillation energy is transformed into the static potential energy.

Thus, the anharmonic oscillator is a specific transformer that converts energy from one type into another.

It is evident that these energy transformations are also valid for zero oscillations of a quantum anharmonic oscillator. This means that the zero energy (which dominates in the oscillation dynamics of solids at temperatures that are fairly low as compared to Debye temperatures) can also be transformed into the static potential energy or can take the potential energy on oscillator loading.

The thermoelastic effect is associated only with changes in the oscillation energy. It should be noted that under real conditions the thermoelastic effect is to a great extent associated with changes in the zero energy. Indeed, in the region of the Debye temperatures (for many solids the Debye temperatures are not far from room temperature), the zero oscillation energy is about a quarter of all the oscillation energy and its fraction grows with decreasing temperature. But because the zero energy E_0 is also proportional to the oscillation frequency ($E_0 = 0.5h\nu$, where h is Planck's constant), its variations on oscillator loading constitute an appreciable fraction of the energy changes of an excited oscillator (changes in the energy level of "thermal" oscillations).

4. Questions arising in the analysis of the behaviour of an anharmonic oscillator

The consideration of the behaviour of an excited anharmonic oscillator on its adiabatic loading explaining the thermoelastic effect by changes in the oscillation frequency of the oscillator, raises some questions.

For instance, the mechanism of conversion of the work of the external force into the oscillation energy on compression is not clear. The same is true for the mechanism underlying conversion of the oscillation energy into static potential energy on extension.

Another important problem is dynamic expansion. The literal interpretation of Eq. (13) and its derivation (minimization of the total energy) lead to the conclusion that excitement of an anharmonic oscillator gives rise to a real extension of the bond, i.e. to the appearance of a static component in the oscillatory deformation of the bond. This points to a displacement of the potential well bottom or a shift in the equilibrium position of a vibrating particle (the position that corresponds to the maximum of the kinetic oscillation energy and zero potential oscillation energy). In its turn, the appearance of a static component of extension requires that a static component of the extending force appears. The question is just how real are both deformation and the force.

It is interesting to note that there is another estimate of the dynamic expansion that coincides quantitatively with the previous one, but has an entirely different meaning [7].

Indeed the elastic force for the potential (2) is

$$F_{\mathrm{el}} = -\frac{\mathrm{d}U}{\mathrm{d}r} = -f(r - r_0) + g(r - r_0)^2 = -f\,\Delta r + g(\Delta r)^2$$

The condition for stability of oscillation is that the time-average force is zero (otherwise the vibrating particle will "leave" the well)

$$\overline{(F_{\mathrm{el}})_t} = -f\overline{\Delta r_t} + g\overline{(\Delta r)_t^2} = 0$$

from here

$$\overline{\Delta r_t} = \frac{g}{f}\overline{(\Delta r)_t^2}$$

$$\bar{\varepsilon}_t = \frac{\overline{\Delta r_t}}{r_0} = \frac{g}{fr_0}\overline{(\Delta r)_t^2}$$

In the harmonic approximation

$$E_{\mathrm{osc}} = f\overline{(\Delta r)_t^2}$$

Then

$$\bar{\varepsilon}_t = E_{\mathrm{osc}}\frac{g}{f^2 r_0}$$

As can be seen, $\bar{\varepsilon}_t$ coincides with ε_0 (Eq. (13)).

However, ε_t defines an average (in time) displacement of a vibrating particle, caused by asymmetry of the well (the result of anharmonicity) in the case of a constant position of the well bottom. But ε_0, as noted above, defines the well bottom displacement. So the problem as to which situation corresponds to the real one remains unresolved.

It is likely that this question could be clarified to some extent by measurements of microexpansion (by X-ray diffraction using the angular position of the reflexes) under the action of fairly large static loads (especially compressing ones).

5. Conclusions

The micromechanism of the thermoelastic effect undoubtedly consists of changes in the oscillation energy of anharmonic oscillators in solids on loading.

At the same time, a number of questions concerning details of the energetics of excited anharmonic oscillators and of the processes occurring on their loading still remain to be solved.

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