The zero static internal stress approximation in lattice dynamics, and the calculation of isotope effects on molar volumes

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For crystals in which relative positions of atoms within the unit cell are not wholly determined by symmetry, a complete application of the quasiharmonic approximation requires the minimization of the free energy with respect to both external (η_λ) and internal (ϵ_j) strains. The zero static internal stress approximation first minimizes the static lattice energy with respect to the ϵ_j for each state of external strain; the total free energy is then minimized only with respect to the η_λ. We show that although this gives an incorrect internal strain, to the first order it gives the correct external strain at each temperature; in principle, errors are thus of the same order as those due to the use of the quasiharmonic approximation. In particular, recent calculations by Lacks [D. J. Lacks, J. Chem. Phys. **103**, 5085 (1995)] of the effect of deuteration on the molar volume of polyethylene are shown by the present analysis to include indirectly the effect of vibrational stretching of the C–H(D) bonds, and their reasonable agreement with room temperature measurements may after all not be fortuitous.
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I. INTRODUCTION

In harmonic lattice dynamics, the vibrational frequencies of a solid are obtained by expanding the potential energy as a Taylor series in terms of the displacements of the atoms from their reference sites, and then taking the normal mode frequencies given by the quadratic terms only. But because the potential energy of a solid is always anharmonic, these frequencies vary with the choice of reference sites. For a perfect crystal, this choice depends upon the external (macroscopic) state of strain of the crystal, and, unless determined by symmetry, also on the relative positions of atoms within the primitive cell (constituting the state of internal strain). The *quasiharmonic* approximation takes the vibrational free energy of the crystal at each such state of strain to be that of a set of harmonic oscillators with these frequencies. It thus allows for the anharmonicity of the crystal potential energy only through the strain dependence of the normal mode frequencies. Nevertheless, it can be shown that to the first order in the anharmonicity this procedure gives the correct vibrational contribution to the pressure, and hence the correct thermal expansion (see, for example, Ref. 1).

In a full application of the quasiharmonic approximation, the free energy is minimized at each temperature with respect to both external and internal strain. To reduce the computational effort required, a further approximation is sometimes used in which the static lattice energy is minimized with respect to internal strain, so that the total free energy has to be minimized only with respect to the external strain.[2–7] We call this *the zero static internal stress approximation*, abbreviated to ZSISA. In this paper we examine its validity. The impetus for this work stems from a recent paper by Lacks,[7] who used the approximation to calculate the effect of deuteration on the molar volume of orthorhombic polyethylene; he found isotopic effects in the a and b lattice parameters to which the C–H/D stretching vibrations contributed strongly. He argued that these were additional to the already known effects due to the vibrational stretching of the C–H/D bonds,[8] because this stretching is an internal strain and is therefore treated by ZSISA only in the static lattice approximation; the internal vibrational stress is neglected. We shall see, however, that this argument is incomplete. Using ZSISA corresponds to a state of the crystal in which not only the internal stress but also the external stress is nonzero; and it turns out that when both these stresses are taken into account, to the first order there is no net effect on the external strain. At high temperatures, or for large zero-point energy, ZSISA may entail errors of the same order as those entailed by the quasiharmonic approximation.

II. FUNDAMENTAL THEORY

It is convenient to use the *general regime*,[9] in which both internal and external strains are treated as thermodynamic variables on the same footing. We denote the external strain by η, comprising a set of coordinates η_λ (with Greek subscripts λ, μ, etc.), and the internal strain by ϵ, comprising a set of coordinates ϵ_j (with Roman subscripts j, k, etc.). Lattice dynamics gives the Helmholtz free energy as a function of these strains,

$$F(\eta,\epsilon,T)=E^{\mathrm{st}}(\eta,\epsilon)+F^{\mathrm{vib}}(\eta,\epsilon,T), \tag{2.1}$$

where st and vib denote static lattice and vibrational contributions, respectively. Conjugate external and internal stresses are then given by

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$$t_\lambda=\frac{1}{V}\left(\frac{\partial F}{\partial \eta_\lambda}\right)_{\eta',\epsilon,T}=t_\lambda^{\rm st}+t_\lambda^{\rm vib};$$
$$\tau_j=\frac{1}{V}\left(\frac{\partial F}{\partial \epsilon_j}\right)_{\eta,\epsilon',T}=\tau_j^{\rm st}+\tau_j^{\rm vib}, \tag{2.2}$$

where the subscripts η' or ϵ' denote that all the η or ϵ are kept constant except for the differentiation variable. When the crystal is in internal equilibrium the τ_j are all zero and the t_λ are the macroscopic stresses. Otherwise, both external and internal stresses depend upon the coordinate system chosen to represent the internal strain (see Sec. III).

At the true minimum of the free energy both t and τ are zero; in contrast, the state selected by ZSISA is given by the conditions

$$\tau_j^{\rm st}=0,\quad \left(\frac{\partial F}{\partial \eta_\mu}\right)_{\eta',\tau^{\rm st},T}=0. \tag{2.3}$$

The first of these conditions shows that the internal stress is given by $\tau_j=\tau_j^{\rm vib}$. The external stress must be derived from the second condition.

Before doing this we must first distinguish between elastic constants in different thermodynamic regimes. In the general regime elastic constants are denoted by script capitals.[9] The isothermal stiffnesses can be obtained by differentiating the computed free energy

$$\mathscr{C}^T_{\lambda\mu}=\frac{1}{V}\left(\frac{\partial^2 F}{\partial\eta_\lambda\partial\eta_\mu}\right)_{\eta',\epsilon,T};\quad \mathscr{C}^T_{\lambda k}=\frac{1}{V}\left(\frac{\partial^2 F}{\partial\eta_\lambda\partial\epsilon_k}\right)_{\eta',\epsilon',T}=\mathscr{C}^T_{k\lambda};$$
$$\mathscr{C}^T_{jk}=\frac{1}{V}\left(\frac{\partial^2 F}{\partial\epsilon_j\partial\epsilon_k}\right)_{\eta,\epsilon',T}. \tag{2.4}$$

Compliances in the general regime are defined by

$$\mathscr{S}^T_{\lambda\mu}=\left(\frac{\partial\eta_\lambda}{\partial t_\mu}\right)_{t',\tau,T};\quad \mathscr{S}^T_{\lambda k}=\left(\frac{\partial\eta_\lambda}{\partial\tau_k}\right)_{t,\tau',T}=\left(\frac{\partial\epsilon_k}{\partial t_\lambda}\right)_{t',\tau,T}=\mathscr{S}^T_{k\lambda};$$
$$\mathscr{S}^T_{jk}=\left(\frac{\partial\epsilon_j}{\partial\tau_k}\right)_{t,\tau',T}. \tag{2.5}$$

They can be computed by inverting the (symmetric) total stiffness matrix $\mathscr{C}^T$; thus

$$\mathscr{S}_{\lambda\mu}\mathscr{C}_{\mu\nu}+\mathscr{S}_{\lambda l}\mathscr{C}_{l\nu}=\delta_{\lambda\nu};\quad \mathscr{S}_{\lambda\mu}\mathscr{C}_{\mu j}+\mathscr{S}_{\lambda l}\mathscr{C}_{lj}=0;$$
$$\mathscr{S}_{j\mu}\mathscr{C}_{\mu k}+\mathscr{S}_{jl}\mathscr{C}_{lk}=\delta_{jk}; \tag{2.6}$$

here and throughout this paper repeated suffices imply summation. The *macroscopic regime* describes laboratory conditions, in which the internal stress is constant (zero). In terms of the general regime, the macroscopic stiffnesses and compliances are therefore given by

$$C^T_{\lambda\mu}=\frac{1}{V}\left(\frac{\partial^2 F}{\partial\eta_\lambda\partial\eta_\mu}\right)_{\eta',\tau,T};\quad S^T_{\lambda\mu}=\left(\frac{\partial\eta_\lambda}{\partial t_\mu}\right)_{t',\tau,T}. \tag{2.7}$$

The first of Eqs. (2.5) show that the macroscopic compliances $S_{\lambda\mu}$ are identical to the compliances $\mathscr{S}_{\lambda\mu}$ in the general regime. Inverting the submatrix $\mathscr{S}_{\lambda\mu}$ thus gives the macroscopic stiffnesses $C_{\lambda\mu}$. Finally,[10] we use gothic letters for a third, *internal*, regime in which the external strain η is held constant. The stiffnesses in this regime are identical to the $\mathscr{C}_{jk}$ in the internal submatrix of the general regime, and the compliances $\mathfrak{S}_{jk}$ can therefore be obtained by inverting this submatrix,

$$\mathscr{C}_{jl}\mathfrak{S}_{lk}=\delta_{jk}. \tag{2.8}$$

We can now return to the second of Eqs. (2.3). By manipulation of partial differentials (see, e.g., Appendix 2 of Ref. 9) it becomes

$$\left(\frac{\partial F}{\partial\eta_\mu}\right)_{\eta',\epsilon,T}+\left(\frac{\partial F}{\partial\epsilon_k}\right)_{\eta,\epsilon',T}\left(\frac{\partial\epsilon_k}{\partial\eta_\mu}\right)_{\eta',\tau^{\rm st},T}=0. \tag{2.9}$$

The derivative $(\partial\epsilon_k/\partial\eta_\mu)_{\eta',\tau^{\rm st},T}$ is purely a property of the static lattice, and so the condition of constant T can be dropped. Equation (2.9) then gives

$$t_\mu=-\tau_k\left(\frac{\partial\epsilon_k}{\partial\eta_\mu}\right)_{\eta',\tau^{\rm st}}, \tag{2.10}$$

where the last derivative can be expanded in the form

$$\left(\frac{\partial\epsilon_k}{\partial\eta_\mu}\right)_{\eta',\tau^{\rm st}}=-\left(\frac{\partial\epsilon_k}{\partial\tau_j^{\rm st}}\right)_{\eta,\tau^{\rm st}'}\left(\frac{\partial\tau_j^{\rm st}}{\partial\eta_\mu}\right)_{\eta',\epsilon}=-\mathfrak{S}^{\rm st}_{kj}\mathscr{C}^{\rm st}_{j\mu}. \tag{2.11}$$

ZSISA is thus seen to correspond to a state under external stresses

$$t_\mu=\tau_k^{\rm vib}\mathfrak{S}^{\rm st}_{kj}\mathscr{C}^{\rm st}_{j\mu} \tag{2.12}$$

since Eqs. (2.2) and (2.3) give $\tau_k=\tau_k^{\rm vib}$. If the solid is now allowed to relax to the true equilibrium, so that the external stress changes by $-t_\mu$ and the internal stress by $-\tau_k$, then to the first order the resultant change in external strain is

$$\Delta\eta_\lambda\approx-\mathscr{S}^T_{\lambda\mu}t_\mu-\mathscr{S}^T_{\lambda l}\tau_l \tag{2.13}$$
$$\approx-\mathscr{S}^T_{\lambda\mu}\mathfrak{S}^{\rm st}_{kj}\mathscr{C}^{\rm st}_{j\mu}\tau_k^{\rm vib}-\mathscr{S}^T_{\lambda l}\tau_l^{\rm vib}. \tag{2.14}$$

Since $\tau_k^{\rm vib}$ is already of the first order, we can neglect the difference between static and isothermal elastic constants, and drop the superscripts T and st. The matrices $\mathscr{C}$ and $\mathscr{S}$ are symmetric by definition [Eqs. (2.4)] and so the second of Eqs. (2.6) enables us to substitute $-\mathscr{S}_{\lambda l}\mathscr{C}_{jl}$ for $\mathscr{S}_{\lambda\mu}\mathscr{C}_{j\mu}$. Using also Eq. (2.8) and the symmetry of $\mathfrak{S}_{jk}$, we find

$$\Delta\eta_\lambda\approx\mathscr{S}_{\lambda l}\mathscr{C}_{jl}\mathfrak{S}_{kj}\tau_k^{\rm vib}-\mathscr{S}_{\lambda l}\tau_l^{\rm vib}\approx\mathscr{S}_{\lambda l}(\delta_{lk}\tau_k^{\rm vib}-\tau_l^{\rm vib})=0 \tag{2.15}$$

confirming that to first order the true equilibrium external strain is the same as that given by ZSISA. However, ZSISA does not give the correct internal strain, for which a similar argument, using the third of Eqs. (2.6), gives

$$\Delta\epsilon_j=-\mathfrak{S}_{jk}\tau_k^{\rm vib}. \tag{2.16}$$

These results are illustrated graphically in Fig. 1. The contours of $E^{\rm st}$ (dotted) and F (continuous) in $\eta-\epsilon$ space are shown for a system with one external and one internal strain coordinate. The continuous line shows the states of strain allowed by ZSISA, joining points on static contours with vertical tangents. The point where this line touches a contour

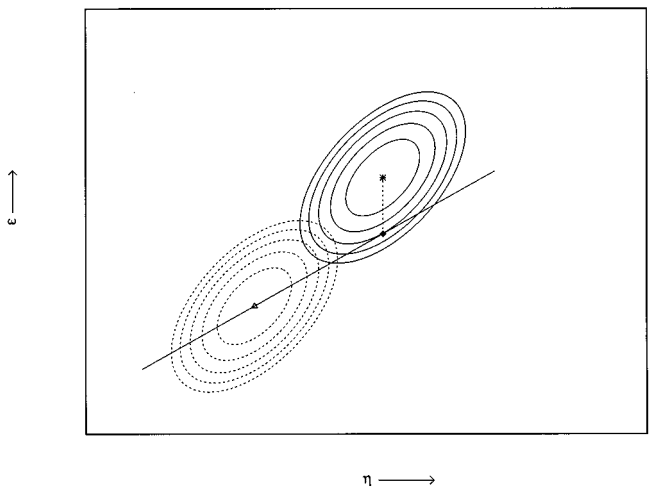

FIG. 1. Energy contours for a system with one external and one internal strain. $\cdots$, E^{st}; —, F. The continuous line shows the states of strain allowed by ZSISA. The point Δ marks the equilibrium state of strain of the static lattice, the point $*$ the true equilibrium at temperature T and the point $\blacklozenge$ the state of strain given by ZSISA.

of F is the state obtained by then minimizing F. To a first approximation the contours are identical sets of similar concentric ellipses, but with different minima, and the continuous line is straight. From this it is straightforward to show analytically, and very easy to show geometrically (by projecting the figure on to a plane such that the ellipses become circles), that the true minimum of F lies directly above this point, giving the same external strain.

The effect that higher order terms will have on the validity of ZSISA is not obvious. We may indeed expect the elasticity of the crystal in its equilibrium state of strain to be softer than that of the static lattice in equilibrium, but provided that all stiffnesses soften proportionately the shape of the contours in Fig. 1 will not alter. The argument remains valid, as can be seen also from Eq. (2.14), where the isothermal stiffnesses will be simply proportional to the static stiffnesses and the compliances will be proportional by a reciprocal factor. In general, however, stiffnesses will not soften proportionately, so that the ellipses will change shape and orientation; furthermore, contours will depart from elliptical shape with increasing distance from the minima. Computations on specific models are needed to investigate when the consequent inaccuracy of ZSISA becomes significant.

III. A ONE-DIMENSIONAL MODEL

The formal analysis given above raises questions of physical interpretation. In particular, what is the nature of the external and internal stresses t_λ and τ_j, and why can they be relaxed from the ZSISA state towards true equilibrium without disturbing the external strain? Such questions are conveniently addressed by taking a specific model.

Consider then the linear chain of diatomic molecules shown in Fig. 2. To relate this model to the energy contours in Fig. 1, we must first define external and internal strain coordinates. The external coordinate is the macroscopic

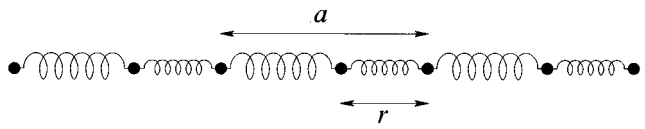

FIG. 2. Linear chain of diatomic molecules.

strain, but the choice of internal coordinate is arbitrary; here we choose it to be the dilation of a molecule. The strain coordinates are then

$$\eta=(a-a_0)/a_0, \quad \epsilon=(r-r_0)/r_0, \tag{3.1}$$

where a_0 and r_0 are the dimensions at the static lattice energy minimum. To the lowest order the intermolecular and intramolecular tensions in the static lattice are then

$$T_\lambda^{\mathrm{st}}=\lambda(a_0\eta-r_0\epsilon), \quad T_\mu^{\mathrm{st}}=\mu(r_0\epsilon), \tag{3.2}$$

where λ and μ are Hooke's Law constants. The static lattice energy per unit length is

$$\frac{1}{2a_0}\left[\lambda(a_0\eta-r_0\epsilon)^2+\mu(r_0\epsilon)^2\right] \tag{3.3}$$

as illustrated by the dotted elliptical contours of Fig. 1. The static stresses t^{st} and τ^{st} (which for a one-dimensional model have the dimensions of force) are obtained by differentiating this expression with respect to η and ϵ, respectively,

$$t^{\mathrm{st}}=\lambda(a_0\eta-r_0\epsilon)=T_\lambda^{\mathrm{st}}, \tag{3.4}$$

$$\tau^{\mathrm{st}}=\frac{1}{a_0}\left[-\lambda r_0(a_0\eta-r_0\epsilon)+\mu r_0^2\epsilon\right]=\frac{r_0}{a_0}\left(T_\mu^{\mathrm{st}}-T_\lambda^{\mathrm{st}}\right). \tag{3.5}$$

We see immediately that the ZSISA condition $\tau^{\mathrm{st}}=0$ is equivalent to $T_\mu^{\mathrm{st}}=T_\lambda^{\mathrm{st}}$, an obvious condition for internal equilibrium, requiring

$$\epsilon=\{\lambda a_0/[(\lambda+\mu)r_0]\}\eta \tag{3.6}$$

and that when the condition is satisfied, t^{st} gives the correct macroscopic static stress. However, when $T_\mu^{\mathrm{st}}\neq T_\lambda^{\mathrm{st}}$ the values not only of τ^{st} but also of t^{st} depend on our original choice of internal strain coordinate; for example, if we had chosen ϵ to be the dilation of the intermolecular springs, the roles of λ and μ would have been interchanged, giving t^{st} equal to T_μ^{st} instead of T_λ^{st}. It follows that t^{st} has a simple physical meaning only if there is internal equilibrium, when the model corresponds to laboratory conditions. Otherwise, the displacement from internal equilibrium must be maintained by additional applied forces (summing to zero) acting on the atoms in each unit cell; the external applied forces then depend on where and how the internal forces are applied. These unphysical stresses arise in calculations either when an approximation like ZSISA is used that forbids the lattice to reach its true internal equilibrium, or when separate stresses are derived from different components of a total free energy.

We next consider the expansion of the lattice caused by the lattice vibrations, and in agreement with Fig. 1 suppose that the anharmonicity of the springs is such that at the new

equilibrium both springs are extended from their original lengths. At the old static lattice equilibrium ($\eta=\epsilon=0$) both springs are now under compression, but the ZSISA condition [Eq. (3.6)] allows them to relax together until the thrust in one of the springs becomes zero. If the thrust in the other spring also becomes zero at this point, the true equilibrium has been reached, but in general this will not be so. In Fig. 1, it is the intermolecular springs that lose their compression first, leaving the intramolecular springs still compressed. The ZSISA free energy can then be reduced further by additional expansion, because initially the work required to stretch the λ-springs will be less than the work obtained from the μ-springs. ZSISA thus finally gives a state in which the molecules are compressed while the intermolecular bonds are under tension. Clearly, when the ZSISA condition is no longer imposed, it is possible for both springs to be at least partly relaxed without altering η. The analysis of Sec. II shows that to the first order the relaxation is complete.

Finally, it is worth noting that if instead of ϵ we take an internal strain coordinate $\tilde{\epsilon}$ that is a measure of the departure from the ZSISA condition, e.g.,

$$\tilde{\epsilon}=\epsilon-\{\lambda a_0/[(\lambda+\mu)r_0]\}\eta, \tag{3.7}$$

the second order expression for the static lattice energy is now diagonal in $\tilde{\epsilon}$ and η, and there is then no elastic coupling between internal and external strains. In $\eta-\tilde{\epsilon}$ space the principal axes of the ellipses become horizontal and vertical, and the line for the ZSISA condition becomes horizontal ($\tilde{\epsilon}=0$). It is then immediately obvious that the point giving the true minimum of F lies directly above the point giving the minimum allowed by ZSISA.

IV. ORTHORHOMBIC POLYETHYLENE

We now return to the calculations[7] which prompted the present work. Previous theoretical estimates of the effect of deuteration on the molar volume of polyethylene had been based on crude arguments which considered only the difference between the C–D and C–H distances. Lacks, assuming the empirical force-field of Karasawa *et al.*,[11] took into account the entire spectrum of lattice vibrations, and used quasiharmonic theory with ZSISA to calculate the equilibrium lattice parameters at $T=0$ (i.e., zero point energy only) and $T=300$ K. An experimental value[12] of 1.0052 for the ratio of molar volumes V_H/V_D at 300 K was in quite close agreement with the value 1.0059 given by the calculations; but it appeared to Lacks that this agreement ''must be considered coincidental, because of the neglect of the differences in the C–H and C–D bond lengths.'' The present analysis shows that this reservation is too strong; to a first approximation ZSISA does allow indirectly (by the addition of fictitious external stresses) for the differences in C–H and C–D bond lengths, and the reasonable agreement Lacks obtained with experiment must be considered encouraging for the model he used.

Finally, we should emphasize that in polyethylene the effect of deuteration involves additional mechanisms besides the simple change of C–H/D bond length suggested by Bartell and Roskos.[8] In addition to possible effects arising from the larger polarizability of the C–H bond, Lacks[7] has drawn attention to the strong temperature dependence of the molar volume isotope effect at temperatures where the C–H/D bond lengths would not be expected to vary appreciably. That this is so should not be surprising, for several reasons.

(i) Although the C–H stretching and bending vibrations will be most affected by deuteration, lower frequency vibrations involving chiefly interchain forces may have larger amplitudes, thus enhancing the effect on interatomic distances.

(ii) Many of the C–H bonds do not point towards the nearest atom in a neighboring chain, making suspect the assumption by Bartell and Roskos[8] that the radius of a cylindrical polymer chain is increased by the increase in bond length.

(iii) The C–H bending vibrations cause the bond to librate, and hence decrease the distance between the mean positions of the C and the H atoms.[13]

Thus not only is the effect of the change in C–H/D bond length on crystal dimensions calculated by ZSISA to a first approximation, but also this effect may not be so great as has hitherto been supposed.

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