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On the mass independence of the mean-square atomic displacement in the classical limit.

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A recent suggestion that the mean-square atomic displacement in the classical limit is mass dependent in the case of a polyatomic crystal is shown to be incorrect.

In a recent article Scheringer (1973) has stated that in the case of a polyatomic crystal, the expression for the mean-square atomic displacement in the classical limit (M.S.D.C.), *i.e.* the linear temperature-dependent term of equation (S1) (we denote equations of Scheringer's article by the prefix S), can be interpreted as signifying a possible experimentally observable mass dependence of the MSDC. Scheringer's discussion is based on the conditions of invariance of the crystal potential energy with respect to rigid translations of the crystal and the fact that these conditions impose mass-dependent conditions on the atomic displacements associated with the zero- and small-wave-vector optical modes. However, aside from the zero-wave-vector contribution to the MSDC which cannot be included in the summation of equation (S1) because the dynamical matrix is singular for zero wave vector, we point out that equations (S1) and (S2) explicitly show that the MSDC depends only on the second-order force constants which of course are mass independent. Furthermore the zero-wave-vector contribution can easily be seen to correspond to a fraction of the MSDC of the order of $1/N$, where N is the number of unit cells of the crystal so this contribution is neglibigle for a macroscopic crystal. The theorem on the mass independence of the MSDC was discussed in the literature some time ago by Blackman (1956) and most recently by Huiszoon & Groenewegen (1972), with whose conclusion Scheringer has incorrectly taken exception.*

Although equations (S1) and (S2) clearly indicate that the total contribution to the MSDC associated with each non-zero wave vector is mass independent, in view of the obvious mass dependence of the small-wave-vector optical contributions as discussed by Scheringer, it is perhaps of some interest to consider the small-wave-vector contribution in some detail. For this purpose it is convenient, although somewhat arbitrary, to appeal to a simple model, namely the diatomic linear chain with nearest-neighbor force constant, β, and to the use of perturbation theory in the secular equations (Born & Huang, 1956; Maradudin, Montroll, Weiss & Ipatova, 1971) Consider the following expression for the contribution to the MSDC at temperature T from the normal mode of wave number q and polarization index j,

$$U_\kappa(T;q,j)=\frac{k_BT}{m_\kappa}\frac{w_\kappa^2(q,j)}{\omega^2(q,j)}\,;\quad \kappa,j=1,2\,. \qquad (1)$$

Here k_B is Bolzmann's constant, m_κ is the mass of the κth atom in the unit cell and $\omega(q,j)$ and $w_\kappa(q,j)$ denote respectively the normal-mode frequency and normalized polarization vector [aside from a simple phase factor (Born & Huang)]. We note further that for this simple model the polarization index distinguishes between acoustical and optical modes only and that the polarization vector is a two-dimensional vector in κ space. Since we wish to evaluate the right-hand side of (1) in the small-q limit we write the dynamical matrix [aside from a simple phase factor (Born & Huang)] in the following manner:

$$C_{\kappa\kappa'}(q)=C^0_{\kappa\kappa'}+C'_{\kappa\kappa'}(q) \qquad (2)$$

where

$$C^0=2\beta\begin{pmatrix}\dfrac{1}{m_1} & \dfrac{-1}{\sqrt{m_1m_2}}\\[2ex] \dfrac{-1}{\sqrt{m_1m_2}} & \dfrac{1}{m_2}\end{pmatrix},$$

$$C'(q)=\frac{2\eta\beta}{\sqrt{m_1m_2}}\begin{pmatrix}0&1\\1&0\end{pmatrix},$$

$$\eta=\frac{(qa)^2}{2}-\frac{(qa)^3}{6}+\ldots,$$

and a is the nearest-neighbor separation (between unlike atoms). Here we have simply expanded the cosine function that appears in the dynamical matrix for this model. Treating $C'_{\kappa\kappa'}(q)$ as a perturbation in the secular equations (Born & Huang; Maradudin *et al.*) equation (1) becomes

$$U_\kappa(T;q,1)=\frac{k_BT}{m_\kappa}\left\{\frac{w_{0\kappa}^2(1)}{\bar{C}'(1,1)}-\frac{2}{\omega_0^2(2)}\frac{\bar{C}'(1,2)}{\bar{C}'(1,1)}w_{0\kappa}(1)w_{0\kappa}(2)+\frac{1}{\omega_0^2(2)}\left[\frac{\bar{C}'(2,1)}{\bar{C}'(1,1)}\right]^2w_{0\kappa}^2(1)+\mathrm{O}(\eta)\right\}$$

$$U_\kappa(T;q,2)=\frac{k_BT}{m_\kappa}\left\{\frac{w_{0\kappa}^2(2)}{\omega_0^2(2)}\right\}+\mathrm{O}(\eta)\,, \qquad (3)$$

where

$$\bar{C}'(j,j')=\sum_{\kappa,\kappa'=1}^{2}w_{0\kappa}(j)C'_{\kappa\kappa'}(q)w_{0\kappa'}(j')\,,$$

$$\omega_0(j)\equiv\omega(0,j),\quad w_{0\kappa}(j)\equiv w_\kappa(0,j)\,,$$

and $j=1,2$ denote acoustical and optical modes respectively. We note that in equations (3) the polarization vector and frequency corresponding to the acoustical mode have been treated up to first-order and second-order perturbation theory respectively. Substituting the expressions

$$\omega_0^2(1)=0,\quad \omega_0^2(2)=2\beta\left(\frac{1}{m_1}+\frac{1}{m_2}\right),$$

$$w_0(1)=\frac{1}{\sqrt{m_1+m_2}}\begin{pmatrix}\sqrt{m_1}\\ \sqrt{m_2}\end{pmatrix}$$

and

$$w_0(2)=\frac{1}{\sqrt{m_1+m_2}}\begin{pmatrix}\sqrt{m_2}\\ -\sqrt{m_1}\end{pmatrix}$$

* During the preparation of this manuscript a rebuttal of Scheringer's article has come to our attention (Groenewegen & Huiszoon (1973). However, we believe that our communication sheds further light on the situation. In particular, in their rebuttal Groenewegen & Huiszoon do not indicate that the mass-dependent contribution (to the MSDC) of the optical modes is cancelled by a corresponding contribution of the acoustical modes.

into equation (3) yields, after some manipulation,

$$U_\kappa(T;q,1)=\frac{k_BT}{\beta}\left\{\frac{1}{4\eta}-\left[\frac{m_{\kappa'}^2}{2}(m_1+m_2)^2-\frac{1}{4}\right]+O(\eta)\right\};\ \kappa'\neq\kappa$$

$$U_\kappa(T;q,2)=\frac{k_BT}{\beta}\left\{\frac{m_{\kappa'}^2}{2(m_1+m_2)^2}+O(\eta)\right\};\ \kappa'\neq\kappa\,.$$

Therefore we have obtained the result, which was to be expected on the basis of the general theorem (Blackman; Huiszoon & Groenewegen), that the mass-dependent contributions to the MSDC of the acoustical small-wave-number modes are identical but of opposite sign to the contributions of the small-wave-number optical modes: the fact that (4) implies that the MSDC is not only independent of m_κ, but also of κ is, of course, a peculiarity of the model we chose. Thus, for example, a model consisting of both first and second-nearest-neighbor interactions, for which the two second-nearest-neighbor force constants (between like atoms) are unequal, yields a κ-dependent MSDC.

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n-Beam lattice images. III. Upper limits of ionicity in $W_4Nb_{26}O_{77}$.

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Corrections are given to Anstis, Lynch, Moodie & O'Keefe [*Acta Cryst.* (1973). A**29**, 138–147].

The title of the paper by Anstis, Lynch, Moodie & O'Keefe (1973) should read '*n*-Beam Lattice Images. III. Upper...'.

Two other corrections should also be made.

Page 139, column two: (ii) under '*Calculations*' should read '(ii) partially ionized $W^{+0.8}$, $Nb^{+1.0}$, $O^{-0.4}$ and $W^{+1.4}$, $Nb^{+1.8}$, $O^{-0.7}$';

Page 144, column one, line 4 should read 'about 100 nm in 3(*g*) and about 120 nm in 3(*h*). At'.

Reference

ANSTIS, G. R., LYNCH, D. F., MOODIE, A. F. & O'KEEFE, M. A. (1973). *Acta Cryst.* A**29**, 138–147.

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Directions of dislocation lines in crystals of ammonium hydrogen oxalate hemihydrate grown from solution: erratum.

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A correction is given to Klapper & Küppers [*Acta Cryst.* (1974). A**29**, 495–503]. In lines 3, 23 and 37 of the Theory and calculations section, in line 11 of the Discussion and in the caption of Fig. 3 $E\cos\alpha$ should read $E/\cos\alpha$ and $K\cos\alpha$ should read $K/\cos\alpha$.

In Klapper & Küppers (1973) the following corrections should be made.

In lines 3, 23 and 37 of the Theory and calculations section, in line 11 of the Discussion and in the caption of Fig. 3 $E\cos\alpha$ should read $E/\cos\alpha$ and $K\cos\alpha$ should read $K/\cos\alpha$.

Reference

KLAPPER, H. & KÜPPERS, H. (1973). *Acta Cryst.* A**29**, 495–503.