

Simple variational approach to the thermal properties of ionic crystals

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Abstract. The thermal properties of ionic crystals are analysed using the variational principle of classical statistical mechanics. The Einstein and Debye pictures of the lattice vibrations are adopted as trial Hamiltonians. No explicit calculation of the lattice spectrum is needed. The variational result for the thermal expansion in the Einstein picture is identical to that recently derived by Narayan and Ramaseshan by a physically motivated thermal force picture. The agreement with experimental values in the alkali halide family of crystals is surprisingly good, the root mean square error being about 14%. The parameters in the interionic potential used are obtained from the lattice spacings and compressibilities of the crystals and not from anharmonic properties. The Debye picture gives about equally good results for the thermal expansion, but better results for the thermal vibration amplitudes of the ions. It differs from the Einstein picture in incorporating correlated vibrations of atoms and in having an explicit Coulomb contribution to the thermal properties. It is suggested that the theory given in this paper has a useful role to play in studies of thermal expansion and phase stability for large families of ionic crystals when combined with semi-empirical theories.

Keywords. Ionic crystals; thermal properties, variational principle.

1. Introduction

Narayan and Ramaseshan (NR) (1980) have recently proposed a computationally simple and physically appealing scheme for calculating the high temperature (classical) thermal expansion of an ionic crystal directly from the interatomic potential without computing the lattice vibration spectrum. The ions are taken to vibrate independently as in an Einstein model and this leads to a mean square vibration amplitude for each type of ion. When averaged over this thermal motion, the force between two ions acquires a 'rectified' component, linear in the temperature, which is introduced into the equation of equilibrium for the crystal. The resulting values of thermal expansion are in good agreement with experiment considering the simplifying assumptions of the theory and the absence of any free parameters. In this paper, we attempt to understand the success of this theory and the nature of the corrections to it.

Our starting point is the variational principle for the free energy in statistical mechanics (reviewed for example in the text book by Feynman (1972)). This variational principle was given by Gibbs (1902) in the classical case and generalised to quantum systems by Peierls (1934). The true Hamiltonian H of the crystal is replaced by a trial Hamiltonian H_0 whose free energy F_0 is known, and which allows us to compute thermal averages exactly. In this paper we choose H_0 corresponding to (a) the Einstein model, specified by force constants k_{\pm} for the two kinds of ions, and (b) the

Debye model, specified by the velocities c_l and c_t of longitudinal and transverse waves. We calculate $\langle H - H_0 \rangle_0$ which is the average of the difference between the true and trial Hamiltonians, computed using H_0 . (The angular brackets denote a thermal average). The variational principle states that we can add $\langle H - H_0 \rangle_0$ to F_0 to get an upper bound for the free energy F of the true Hamiltonian H .

$$F \leq F_0 + \langle H - H_0 \rangle_0 = \langle H \rangle_0 - TS_0, \quad (1)$$

S_0 is the entropy corresponding to H_0 given by $TS_0 = \langle H_0 \rangle_0 - F_0$. Minimising the right hand side of (1) with respect to the parameters k_{\pm} (for the Einstein model) or $c_{l,t}$ (for the Debye model) gives us the best value of the free energy, though not necessarily of its derivatives. We discuss the Einstein model in the next section and the Debye model in § 3.

2. The Einstein model

The entropy of an oscillator of mass m , force constant k and frequency ν is given by

$$S = k_B \ln \left(\frac{T}{\nu} \right) = k_B \ln \left(\frac{T}{2\pi} \sqrt{\frac{m}{k}} \right), \quad (2)$$

where k_B is the Boltzmann's constant. Here and later we omit terms not depending on the lattice spacing since these do not affect thermal expansion. For the same reason the kinetic energy is also omitted in what follows. By the earlier discussion, the trial free energy using the Einstein model is given by

$$F_t = \langle H \rangle_0 - 3 N k_B T \left(\frac{1}{2} \ln k_+ + \frac{1}{2} \ln k_- \right) \quad (3)$$

where N is the number of ion pairs in the crystal. We need to evaluate $\langle H \rangle_0$ which is the true crystal potential averaged over the motion of Einstein oscillators. For this we introduce $x_{\pm}, y_{\pm}, z_{\pm}$, the Cartesian components of the displacements of positive and negative ions from their sites in the lattice. As is usual in lattice dynamics, we expand the potential energy as a function of these displacements, the zero order term being the potential energy of the ideal static lattice.

$$U = U_0(r) + li. + qd. + cu. + qt. + \dots \quad (4)$$

In (4) we have just indicated schematically the terms which are linear, quadratic, cubic and quartic in the displacements. The linear terms vanish in the high symmetry structures such as NaCl and CsCl which are considered here. Since we need the thermal average of (4), clearly the cubic terms do not contribute. The mean square of any Cartesian component of the displacement of the ion is given by $k_B T/k_{\pm}$ for the Einstein model, while the product of two different components or the displacements of two different ions averages to zero. Thus among the quadratic terms in (4), only those of the form $\sum_i (x_i^2 + y_i^2 + z_i^2)_{\pm}$ survive. The coefficient of

such a term is the second derivative of the potential energy of the crystal with respect to the displacement of one atom, the others being held fixed. This is just the quantity which occurs in the NR theory and is easily calculated as follows. Let W_{\pm} be the combined repulsion and van der Waals energy for a nearest neighbour unlike ion pair (separated by r) and W_{++} and W_{--} that for second neighbour like ion pairs (separated by $2br$). Let n_1 and n_2 denote the number of first and second neighbours (taken to be the same for both types). The average of the quadratic terms is then found to be

$$\langle qd \rangle_0 = \frac{Nn_1}{2} (\nabla^2 W_{\pm})_r \left(\frac{k_B T}{k_+} + \frac{k_B T}{k_-} \right) + \frac{Nn_2}{2} \left\{ (\nabla^2 W_{++})_{2br} \frac{k_B T}{k_+} + (\nabla^2 W_{--})_{2br} \frac{k_B T}{k_-} \right\}. \quad (5)$$

In equation (5) the potential W_{+-} between nearest neighbours is to be evaluated at r , while W_{++} and W_{--} , which act between second neighbours, are to be evaluated at $2br$. This is also true of the derivatives of the potential with respect to distance like $\nabla^2 W_{+-}$, etc., as indicated by the suffixes r and $2br$. There is no contribution to (5) from the Coulomb potential since its Laplacian vanishes.

Liebfried and Ludwig (1961) have shown that the contribution of the quartic terms to the free energy is of order $(k_B T)^2$. As also discussed by these authors, there is a contribution to the free energy, also of order $(k_B T)^2$, coming from the *square* of the cubic term. This is a fluctuation effect not included in the right side of equation (1). We therefore choose to exclude the contributions of the quartic terms from this point. Substituting (5) and (4) into the trial free energy (3) one obtains

$$F_t = U_0(r) + \frac{Nn_1}{2} (\nabla^2 W_{+-}) \left(\frac{k_B T}{k_+} + \frac{k_B T}{k_-} \right) + \frac{n_2 N}{2} \left[(\nabla^2 W_{++}) \left(\frac{k_B T}{k_+} \right) + (\nabla^2 W_{--}) \left(\frac{k_B T}{k_-} \right) \right] - 3N \frac{k_B T}{2} (\ln k_+ + \ln k_-). \quad (6)$$

We minimise F_t with respect to the parameters k_+ and k_- to obtain the "best" free energy F_v . The result is

$$k_+ = \frac{n_1 \nabla^2 W_{+-} + n_2 \nabla^2 W_{++}}{3} \equiv K_+, \quad (7a)$$

$$k_- = \frac{n_1 \nabla^2 W_{+-} + n_2 \nabla^2 W_{--}}{3} \equiv K_-, \quad (7b)$$

$$F_v = U_0(r) - \frac{3Nk_B T}{2} (\ln K_+ + \ln K_-). \quad (7c)$$

Terms not depending on r have been omitted in (7c). Minimising the variational free energy F_v with respect to r gives the equilibrium lattice spacing at each tempera-

ture and differentiating this equilibrium condition with respect to T gives the thermal expansion. The result is

$$\alpha = \frac{1}{r} \frac{dr}{dT} = \frac{-3k_B (K'_+/K_+ + K'_-/K_-)}{2r \left[U_0''(r) + \frac{3k_B T}{2} \left(\frac{K_+ K_+'' - K_+'^2}{K_+^2} + \left(\frac{K_- K_-'' - K_-'^2}{K_-^2} \right) \right) \right]} \quad (8)$$

where the primes denote differentiation with respect to r , the nearest neighbour distance. This is the equation derived by NR from their intuitive force picture, now emerging from a variational free energy picture. Strictly speaking one should omit the term of order $k_B T$ in the denominator of (8) since neglected effects such as the cubic and quartic terms in the potential also give contributions of the same order. However, these terms represent a well-defined physical effect, *viz.*, the temperature dependence of the (quasi) harmonic frequencies induced by the volume change. We have chosen to retain this term and compare with the room temperature data for reasons explained in section 4.

3. The Debye model

We next consider the Debye picture of lattice vibrations, with a doubly degenerate transverse branch with frequency $\omega = c_t k$ and a longitudinal branch with $\omega = c_l k$, both terminating at $k = k_D$, the Debye cut off wave vector. In such a description, the optical modes of the crystal lying in the second Brillouin zone are being approximated by those modes which lie in the outer half of the volume of the Debye sphere in k -space. The Debye approximation undoubtedly overestimates the dispersion of these modes just as the Einstein model neglects dispersion altogether. These two extremes may be expected to bracket the real situation. We thus have, equating the total number of modes to the number of degrees of freedom,

$$3 \cdot \frac{4\pi}{3} (k_D/2\pi)^3 = 6N \quad (9)$$

Here N is the number of ion pairs per unit volume. For convenience we relate the volume per ion pair v to the nearest neighbour distance r by setting $v = \lambda r^3$. ($\lambda = 2$ for the NaCl structure and $(8/3\sqrt{3})$ for the CsCl structure). The new features introduced in the Debye picture are (a) There is correlation between the displacements of different atoms and so we need to retain terms involving products of two such displacements when we average equation (4). (b) The second derivatives of the potential parallel and perpendicular to a bond no longer occur with equal coefficients since longitudinal and transverse waves travel with different velocities (for details see the Appendix). Thus, even the Coulomb interaction makes a contribution. (c) Anions and cations have the same amplitude of vibration since the Debye model envisages an elastic continuum in which they move together. However, we expect on physical grounds that the predicted vibration amplitudes will be greater than in the Einstein picture since neighbouring atoms can now move coherently and there-

fore out of each other's way. The detailed calculation of the variational free energy for the Debye model is given in the Appendix and we only quote here the final result for the thermal expansion. First we define two quantities K_l and K_t with dimensions of energy length⁻² which play the same role for longitudinal and transverse waves as K_{\pm} do in the Einstein model for the vibrations of positive and negative ions.

$$K_l = l_1 W''_{+-} + l_2 \frac{W'_{+-}}{r} + l_3 (W'_{++} + W'_{--}) + l_4 \left(\frac{W'_{++}}{R} + \frac{W'_{--}}{R} \right) - \frac{Ce^2}{r^3},$$

$$K_t = t_1 W'_{+-} + t_2 \frac{W'_{+-}}{r} + t_3 (W'_{++} + W'_{--}) + t_4 \left(\frac{W'_{++}}{R} + \frac{W'_{--}}{R} \right) + \frac{Ce^2}{r^3} \quad (10)$$

$R = 2br =$ second neighbour distance.

The numerical coefficients $l_1 - l_4$, $t_1 - t_4$ and C are tabulated in the Appendix for the two structures of interest—NaCl and CsCl. They are related to the correlation function (in the Debye model) for longitudinal and transverse vibrations of atoms. In terms of K_l and K_t the final formula for the thermal expansion α has a very similar structure to (8)

$$\alpha = -k_B \frac{\left[\frac{K'_l}{K_l} + \frac{2K'_t}{K_t} \right]}{r \left[U''_0(r) + k_B T \left\{ \frac{K_l K''_l - K_l'^2}{K_l^2} + 2 \frac{K_t K''_t - K_t'^2}{K_t^2} \right\} \right]} \quad (11)$$

4. Comparison with experiment

Table 1 shows the results of calculations with equations (8) and (11) compared to the measured values of 3α (volumetric expansion) in crystals of the alkali halide family. The repulsion potential used is that of Narayan and Ramaseshan (1977, 1978) which is derived from the lattice spacings and compressibilities of these crystals. Thus there is no input based on anharmonic properties at all. Wherever experimental data are available for the mean square vibration amplitudes of atoms in these crystals, we have compared them to the calculated values. The overall agreement in both the theories is good, with the Einstein model results for α being in fact better! However, one must bear in mind that obtaining theoretical values at room temperature would require determining terms of order $(k_B T)^2$ in the free energy. As mentioned before (6) this cannot be done within the variational framework. One can of course extrapolate the measured data to absolute zero to obtain the classical crystal values. We have not performed the detailed fits required for this purpose which involve separating or allowing for the quantum regime as well as the higher temperature regime in which terms of order $(k_B T)^3$ in the free energy enter (Leadbetter *et al* 1969). A quick look at the data suggests that the values extrapolated to 0°K would be about 10% to 20% lower than the room temperature values. Thus it is possible that the Debye theory is giving us marginally better agreement than the Einstein theory. It is also clear that the errors are not random, varying systematically across the family.

Table 1. Comparison of the Einstein theory and the Debye theory with experiment for the volumetric expansion 3α and the root mean square vibration amplitude $\sqrt{\bar{x}^2}$. The suffixes \pm refer to the cation and anion. (The Debye theory predicts equal amplitudes for both).

Crystal	Structure	Experimentals ^a $3\alpha \times 10^4$	Errors in calculated 3α (%)			Experimental rms amplitudes (Å)		Calculated Amplitude (Å)		
			Einstein equation (8)	Debye equation (11)	Simple Theory equation (13)	$\sqrt{\bar{x}_+^2}$	$\sqrt{\bar{x}_-^2}$	$\sqrt{\bar{x}_+^2}$	Einstein $\sqrt{\bar{x}_-^2}$	Debye $\sqrt{\bar{x}_-^2}$
LiF	NaCl	0.92	-2.9	-9.2	-15.9			0.088	0.071	0.104
LiCl	NaCl	1.22	-6.2	-12.8	-22.0			0.128	0.092	0.138
LiBr	NaCl	1.40	-10.4	-16.7	-27.1			0.148	0.103	0.154
LiI	NaCl	1.67	-13.4	-19.0	-32.8			0.185	0.121	0.183
NaF	NaCl	0.98	0.6	-5.8	-7.7		0.104 ^b	0.095	0.086	0.123
NaCl	NaCl	1.10	5.0	-1.2	-3.6		0.142 ^c	0.118	0.101	0.147
NaBr	NaCl	1.19	-0.1	-6.1	-6.6			0.125	0.104	0.154
NaI	NaCl	1.35	1.3	-4.5	-9.9			0.153	0.123	0.182
KF	NaCl	1.00	3.3	-4.9	3.0			0.101	0.097	0.139
KCl	NaCl	1.01	21.8	14.2	16.1		0.165 ^c	0.119	0.111	0.161
KBr	NaCl	1.10	14.8	7.7	11.3			0.126	0.116	0.169
KI	NaCl	1.25	9.1	2.5	4.6			0.141	0.128	0.186
RbF	NaCl	0.95	7.1	-1.3	11.2			0.096	0.092	0.134
RbCl	NaCl	0.99	26.2	18.5	22.4			0.116	0.110	0.160
RbBr	NaCl	1.04	26.7	19.0	21.7		0.170 ^d	0.125	0.118	0.172
RbI	NaCl	1.19	12.7	5.8	11.9			0.133	0.124	0.181
CsF	NaCl	0.95	-10.2	-19.8	17.6			0.093	0.092	0.133
CsCl	CsCl	1.37	-23.8	-29.0	-5.1		0.149 ^{e,f}	0.116	0.111	0.152
CsBr	CsCl	1.39	-16.9	-22.0	-3.3		0.158 ^f	0.124	0.114	0.159
CsI	CsCl	1.46	-16.2	-21.4	-3.5		0.167 ^f	0.132	0.117	0.166
rms error %			14.1	14.5	15.5			26.2		8.1
Mean error %			1.4	-5.3	-0.9			-25.1		1.8

a: Tosi (1964); b: Sharma (1974); c: Viswamitra and Jayalakshmi (1970); d: Jarvinen and Inkinen (1967); e: Barnea and Post (1966); f: Agarwal *et al* (1975).

While we have no explanation for this systematic variation, it is worth noting that the thermal expansion is dominated by the third derivative of the repulsion energy [from the K' terms in (8) and (11)]. The lattice spacing and compressibility determine only the first two derivatives, and the third derivative used is obtained from these by assuming an exponential form for the potential for all the ions. For example, the $(1/r)^n$ form of repulsion would give a third derivative higher by $1/n$ i.e., approximately 10%. It is therefore surprising that such a simple form of the potential combined with the simplified theory of this paper can give agreement at the 15% level. Certainly, it will require more accurate potentials, quite apart from a more refined theory, to improve this agreement. Some of the available data on atomic vibrations in the alkali halides are given in table 1. These can be compared with the root mean square amplitudes of vibration at 300 K for the anion and cation of each crystal, calculated both in the Einstein and Debye pictures. As expected, the vibration amplitudes are too low in the Einstein picture, while the Debye picture, which allows for correlated motion of neighbours, gives results closer to experiment. On the other hand, the Debye model forces the amplitudes of vibration of anion and cation to be equal while the Einstein model can give different values especially when second neighbour effects become important. (For a model with only nearest neighbour and Coulomb forces the two amplitudes are rigorously equal in the classical, high temperature regime). In general, the experimental vibration amplitudes are nearly equal for the two ions, once again suggesting that the Debye theory is better. It is interesting that the 25% lower vibration amplitude in the Einstein model has *not* led to a corresponding systematic error in the thermal expansion. This is because the "thermal pressure" tending to dilate the crystal depends not only on vibration amplitudes but on correlations as well and the combined effect of these two on the thermal expansion (or more strictly on the free energy) has come out correctly thanks to the variational principle.

5. Simplified form of the theory

In the expressions (8) and (11) for the thermal expansion, we find derivatives of the potential to various orders. In the pair potentials W_{+-} , W_{++} and W_{--} , the leading term is the repulsion which is usually modelled in the form of $\exp(-r/\rho)$ where ρ is a constant for each crystal. Neglecting the van der Waals interaction and the second neighbour repulsion, each differentiation of the pair potential generates an extra $1/\rho$ which implies, from dimensional considerations, an extra factor $1/\gamma = r/\rho$. This quantity (which corresponds to the exponent n in the $1/r^n$ form of repulsion energy) takes values near 10 in the alkali halides family. We can separate a zero order term and one of order γ in the expressions (8) and (11) for the thermal expansion. The zero order term is the same in the Einstein and Debye models and indeed represents a general result as we show later below.

Consider now a crystal with only nearest neighbour repulsion $W_{+-} = A \exp(-r/\rho)$. It is easy to compute the thermal expansion from (8). Retaining only terms up to order γ , we find

$$K'_+/K_+ = K'_-/K_- = -1/\rho.$$

Denoting the Madelung constant by a_M , the denominator of (8) at 0°K reads

$$U_0''(r) = -\frac{2a_M e^2}{r^3} + \frac{n_1}{\rho^2} A \exp(-r/\rho).$$

From the equilibrium condition

$$a_M e^2/r^3 = \frac{n_1}{\rho} A \exp(-r/\rho). \quad (12)$$

(The error introduced by using the zero temperature equilibrium condition is of a higher order in $k_B T$). Hence the thermal expansion takes the strikingly simple form

$$\alpha = \frac{3k_B/\rho}{r\left(-\frac{2a_M e^2}{r^3} + \frac{a_M e^2}{r^2 \rho}\right)} = \frac{3k_B}{a_M e^2} (r + 2\rho) = 1000 r (1 + 2\gamma). \quad (13)$$

The Madelung constant has been taken to be 1.75 which is nearly the same for both the NaCl and CsCl structures. The values of thermal expansion calculated with equation (13) are shown in table 1.

In the Debye picture, we similarly find

$$\frac{K'_l}{K_l} = -\frac{1}{\rho} \left[1 + \frac{Cn_1}{l_1 a_M} \gamma \right]; \quad \frac{K'_t}{K_t} = \frac{-1}{\rho} \left[1 - \frac{Cn_1}{l_1 a_M} \gamma \right] \quad (14)$$

$$\begin{aligned} \alpha &= \frac{3k_B}{a_M e^2} \left[r + \rho \left[2 - \frac{Cn_1}{3a_M} \left(\frac{2}{l_1} - \frac{1}{l_1} \right) \right] \right] \\ &= 1000 r (1 + 1.147 \gamma) \text{ for NaCl and } 1000 r (1 + 1.030 \gamma) \text{ (CsCl)} \end{aligned} \quad (15)$$

The effect of the Coulomb contribution as estimated by the Debye model is to lower the thermal expansion, as seen by comparing (15) and (13). The leading term is however the same as that in the Einstein model, *viz.*, $\alpha = 1000r$ and this leads one to suspect that this is a model independent result.

To derive this we note that to order $k_B T$, the free energy is correctly given by the quasiharmonic approximation (Liebfried and Ludwig 1961), where we only take the volume dependence of the harmonic frequencies into account. In this approximation, the entropy is given by

$$\sum_i k_B \ln \left(\frac{k_B T}{h\nu_i} \right)$$

(where the summation is over the modes of the crystal) and the internal energy by the equipartition value. From the equilibrium condition $\partial F/\partial r = 0$ we get

$$\sum_i (k_B T) \frac{1}{\nu_i} \left(\frac{\partial \nu_i}{\partial r} \right) + 2N \frac{\partial U_0(r)}{\partial r} = 0,$$

and on differentiating with respect to temperature,

$$-k_B \sum_i \frac{1}{\nu_i} \frac{\partial \nu_i}{\partial r} + \frac{\partial^2 U_0(r)}{\partial r^2} \frac{dr}{dT} = 0,$$

$$\text{i.e. } a = \frac{1}{r} \frac{dr}{dT} = \frac{k_B}{r} \frac{\sum_i \frac{1}{\nu_i} \frac{\partial \nu_i}{\partial r}}{2N U_0''(r)}. \quad (16)$$

The dependence of the individual frequencies ν_i upon the lattice spacing r is different but we need only an average over the whole spectrum. We can evaluate this as follows

$$\sum_i \frac{\partial}{\partial r} \ln \nu_i = \frac{\partial}{\partial r} \sum_{\mathbf{k}} \ln \det M(\mathbf{k}), \quad (17)$$

where $M(\mathbf{k})$ is the dynamical matrix whose eigenvalues give the frequencies of the different lattice modes (in this case six) at wave vector \mathbf{k} . A typical element of this matrix is, for example, the force on the anion in the x -direction per unit displacement of the cation lattice in the y -direction, modulated at wave vector \mathbf{k} . All we need to note is that this has contributions from both the short-range repulsion and the Coulomb force, which vary as $(A/\rho^2) \exp(-r/\rho)$ and De^2/r^3 (D is a dimensionless lattice sum). In comparing the two terms we can again use the equilibrium condition [equation (12)] to conclude that the Coulomb contributions to the dynamical matrix are of order γ compared to those from short-range repulsion. To the lowest order in γ , we then find that $(1/\nu_i) (\partial \nu_i / \partial r) = -1/\rho$ for all modes. Returning to (16), the thermal expansion is given by

$$a = \frac{3k_B}{\alpha_M e^2} r, \quad (18)$$

which is identical to the zero order term in (8), (11) and (13). We thus conclude that the success of the Einstein or Debye pictures in spite of the simplified view they take of the lattice spectrum is based on the smallness of ρ/r ($\approx 1/10$) as well as the ability of the variational principle to come up with optimal values of the parameters in these pictures.

6. Conclusions

The main result of this paper is that the physically motivated, approximate theory of thermal effects in ionic crystals given by Narayan and Ramaseshan (1980) can be derived from the variational principle of statistical mechanics and usually gives results in error by not more than about 10–15%. The ion-dependent approach to repulsion developed by these authors (Narayan and Ramaseshan (1976, 1977, 1978)) enables predictions to be made for crystals and structures other than those used to fit the parameters of the theory. This predictive power can now be extended to thermal effects with some confidence, without either new parameters or elaborate calculations. Possible applications include thermal expansion and temperature induced transformations. The theory given in this paper is of course not a substitute for more sophisticated theories of anharmonicity (Cowley and Cowley 1965; Barron and Klein 1974) but fits well into the framework of semiempirical theories, such as that of Narayan and Ramaseshan, which attempt to explore the systematics of the entire family of ionic crystals in a conceptually and computationally simple way.

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Appendix

Displacement correlation function and free energy for Debye model

Consider a longitudinal elastic wave of wave vector \mathbf{k} and maximum displacement u_l , propagating with velocity c_l along a direction making polar angles (θ, ϕ) with the z -axis. Two atoms separated by a distance R along the z axis undergo oscillations along z given by $u_z(0) = u_l \cos \theta \cos \omega t$ and $u_z(R) = u_l \cos \theta \cos(\omega t - k R \cos \theta)$. We are interested in the correlation $\phi_l(R)$ between the displacements $u_z(0)$ and $u_z(R)$ of two atoms separated by R . The contribution of this wave to the mean square displacement $\phi(0)$ is $\frac{1}{2} u_l^2 \cos^2 \theta$ and to the longitudinal displacement correlation function $\phi_l(R) = \langle u_z(0) u_z(R) \rangle$ is $\frac{1}{2} u_l^2 \cos^2 \theta \cos(k R \cos \theta)$. The contribution to the transverse correlation function $\langle u_x(0) u_x(R) \rangle$ is $\frac{1}{2} u_l^2 \sin^2 \theta \cos^2 \phi \cos(k R \cos \theta)$. In thermal equilibrium there are no phase correlations between different modes and their contributions to the mean square amplitude and correlation function can be added. The average kinetic energy in a mode of angular frequency ω is $\frac{1}{2} M (\omega^2 u^2/2)$ where M is the mass of the crystal and ωu the velocity amplitude. From the equipartition law $u^2 = 2 k_B T/M\omega^2 = 2 k_B T/Mc^2 k^2$ for a mode of velocity c .

By similar arguments, we can find the contribution of the two degenerate transverse modes of wave vector \mathbf{k} to $\phi(0)$, $\phi_l(R)$ and $\phi_t(R)$. These are $\frac{1}{2} u_l^2 \sin^2 \theta$, $\frac{1}{2} u_l^2 \sin^2 \theta \cos(k R \cos \theta)$ and $\frac{1}{2} u_l^2 (1 - \sin^2 \theta \cos^2 \phi) \cos(k R \cos \theta)$. Combining all contributions for a crystal of volume V we have

$$\begin{aligned} \phi_l(R) = \frac{k_B T}{M} \frac{V}{(2\pi)^3} \int d^3 \mathbf{k} & \left[\frac{1}{c_l^2 k^2} \cos^2 \theta \cos(k R \cos \theta) \right. \\ & \left. + \frac{1}{c_t^2 k^2} \sin^2 \theta \cos(k R \cos \theta) \right] \end{aligned} \quad (19)$$

$$\begin{aligned} \phi_t(R) = \frac{k_B T}{M} \frac{V}{(2\pi)^3} \int d^3 \mathbf{k} & \left[\frac{\sin^2 \theta \cos^2 \phi}{c_l^2 k^2} \cos(k R \cos \theta) \right. \\ & \left. + \frac{(1 - \sin^2 \theta \cos^2 \phi)}{c_t^2 k^2} \cos(k R \cos \theta) \right]. \end{aligned} \quad (20)$$

The integrals over θ and ϕ can be done, leaving one over $u = kR$ from 0 to $k_D R$ where k_D is the Debye cut-off wave vector. We can also use the mass per ion pair m and the volume per ion pair λr^3 . For the mean square displacement, $\phi_l(0) = \phi_t(0)$ is used. The result is

$$\phi_l(R) = \frac{k_B T}{m} \frac{\lambda r^2}{4\pi^2} \left(\frac{r}{R} \right) \left[\frac{2I_0 - 4I_1}{c_l^2} + \frac{4I_1}{c_t^2} \right], \quad (21)$$

$$\phi_t(R) = \frac{k_B T}{m} \frac{\lambda r^2}{4\pi^2} \left(\frac{r}{R} \right) \left[\frac{2I_1}{c_l^2} + \frac{2I_1 - 2I_0}{c_t^2} \right]. \quad (22)$$

$$\phi(0) = \frac{(k_D r)}{6\pi^2} \frac{k_B T}{m} \lambda r^2 \left[\frac{1}{c_l^2} + \frac{2}{c_t^2} \right], \quad (23)$$

where

$$I_0(R) = \int_0^{k_D R} \frac{\sin u}{u} du, \quad I_1(R) = \int_0^{k_D R} \frac{\sin u - u \cos u}{u^2} du$$

$$I_0(\infty) = 2 I_1(\infty) = \pi/2, \quad k_D R = 3.89778 \text{ (NaCl)} = 4.25296 \text{ (CsCl)}.$$

It is easy to see that $u_x(0)$ and $u_{z,y}(R)$ are uncorrelated. With the help of the above correlation functions, we can compute the trial free energy in the Debye model. Consider a "bond" of length R , lying in the z direction, joining a pair of atoms with displacements, $x_1 y_1 z_1$ and $x_2 y_2 z_2$. Let the potential V between these atoms be expressed as a function of the relative displacement

$$x = x_2 - x_1, \quad y = y_2 - y_1, \quad z = z_2 - z_1.$$

The quadratic terms in the energy read

$$\frac{1}{2} \frac{\partial^2 V}{\partial x_1^2} x_1^2 + \dots \frac{\partial^2 V}{\partial x_1 \partial x_2} x_1 x_2 + \dots \quad (24)$$

The derivatives with respect to x_1, x_2 , etc., can be expressed in terms of those with respect to x, y, z . After averaging, products like $x_1 x_2$ and $z_1 z_2$ get replaced by the corresponding correlation functions ϕ_t and ϕ_l and we obtain

$$\frac{1}{2} \left(\frac{\nabla^2 V}{3} \right) \phi(0) - \frac{\partial^2 V}{\partial z^2} \phi_l(R) - \frac{\partial^2 V}{\partial x^2} \cdot 2 \phi_t(R). \quad (25)$$

Since the longitudinal and transverse correlations are unequal, the latter two terms in the above equation do not reduce to $\nabla^2 V$ and therefore the Coulomb interaction contribution does not vanish.

The remaining steps in the derivation of the free energy are quite similar to the Einstein case, including the minimisation with respect to the characteristic frequencies (c_t/r) and (c_l/r) which enter *via* ϕ_l and ϕ_t .

The entropy term reads

$$-TS = -2Nk_B T \left[\ln \left(\frac{c_t}{r} \right) + 2 \ln \left(\frac{c_l}{r} \right) \right], \quad (26)$$

and the energy term reads

$$\begin{aligned} \langle H \rangle_0 = & \frac{Nk_B T}{M} \frac{\lambda}{4\pi^2} \left\{ n_1 \left[V_{rr} \left(\frac{\frac{2}{3}(k_D r) - 2I_0(r) + 4I_1(r)}{(c_l/r)^2} \right) \right. \right. \\ & + \frac{\frac{4}{3}(k_D r) - 4I_1}{(c_l/r)^2} \left. \right] + \frac{V_r}{r} \left(\frac{\frac{2}{3}(k_D r) - 2I_1(r)}{(c_l/r)^2} \right) \\ & + \left. \frac{\frac{4}{3}(k_D r) - 2I_0(r) + 2I_1(r)}{(c_l/r)^2} \right] \\ & + n_2 \text{ (a similar term for second neighbours)} \left. \right\}. \quad (27) \end{aligned}$$

The potential V in (27) can be taken as W_{+-} in the first term, W_{--} and W_{++} in the second. The Coulomb term has the same basic structure as (25). It is a sum involving the correlation functions $\phi_l(R)$ and $\phi_t(R)$ given in (21) and (22) for all neighbours. In our calculations, we have replaced I_0 and I_1 by their asymptotic forms beyond second neighbours and by their computed values (from (23)) for the first and second neighbours. The Coulomb contribution to the trial free energy then reads

$$\langle H_{\text{coulomb}} \rangle_0 = \frac{Nk_B T}{M} \frac{\lambda}{4\pi} \frac{e^2}{r^3} C' \left(\left(\frac{c_t}{r} \right)^{-2} - \left(\frac{c_l}{r} \right)^{-2} \right).$$

Here C' is a lattice sum in which the distant terms have a $\pm 1/R^4$ dependence coming from $\pm 1/R^3$ (second derivative of the Coulomb potential) and $1/R$ (asymptotic behaviour of correlations in the Debye model).

Defining $K_l = m \left(\frac{c_l}{r} \right)^2$, $K_t = m \left(\frac{c_t}{r} \right)^2$, $C = \frac{C'\lambda}{4\pi}$ we minimise the free energy expressions (26) and (27) with respect to K_l and K_t to obtain

$$K_l = m \left[l_1 W''_{+-} + l_2 \frac{W'_{+-}}{r} + l_3 (W''_{++} + W''_{--}) + l_4 \left(\frac{W'_{++}}{R} + \frac{W'_{--}}{R} \right) + \frac{Ce^2}{r^3} \right]$$

$$K_t = m \left[t_1 W''_{+-} + t_2 \frac{W'_{+-}}{r} + t_3 (W''_{++} + W''_{--}) + t_4 \left(\frac{W'_{++}}{R} + \frac{W'_{--}}{R} \right) - \frac{Ce^2}{r^3} \right].$$

The coefficients $l_1 - l_4$, $t_1 - t_4$ and C are tabulated in table 2 for the two structures of interest. The free energy corresponding to the above values of K_l and K_t leads to the thermal expansion coefficient α given in (11) of the main text.

Table 2. Some numerical coefficients used in the Debye theory (equation (10))

	NaCl	CsCl
l_1	0.7039	0.8504
l_2	0.5855	0.7380
l_3	0.8557	0.3481
l_4	0.8832	0.3294
t_1	0.5855	0.7380
t_2	1.9932	2.4389
t_3	0.8832	0.3295
t_4	2.5945	1.0256
C	0.3741	0.4148

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