Appendix to Gory

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Abstract

This document contains a few standard bits of theory written in the language of [1], henceforth referred to as I. On the whole these were originally written for inclusion in I but were excised as being unnecessary.

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Contents

1 Statistical mechanics of the vibrational quantities

Presented here are the standard statistical mechanical manipulations leading to expressions for the energy, entropy, etc.

From diagonalising the dynamical matrix the mode frequencies $\omega_{\mathbf{q}s}$ are obtained.

The allowed energy levels for a mode of frequency $\omega_{\mathbf{q}s}$ are $(1/2+n)\hbar\omega_{\mathbf{q}s}$, contributing a factor to the partition function

$$\begin{aligned} Z_{\mathbf{q}s} &= \sum_n e^{-\left(\frac{1}{2}+n\right)\beta\hbar\omega_{\mathbf{q}s}} \\ &= \frac{e^{-\frac{1}{2}\beta\hbar\omega_{\mathbf{q}s}}}{1-e^{-\beta\hbar\omega_{\mathbf{q}s}}} \qquad (1) \end{aligned}$$

where k_B is Boltzmann's constant and $\beta = 1/k_BT$. Standard thermodynamic and statistical mechanical manipulations then lead to mode contributions for the entropy S, Helmholtz free energy F, internal energy U and constant volume heat capacity C_v of

$$\begin{aligned}
F_{\mathbf{q}s} &= -k_B T \ln Z_{\mathbf{q}s} && (2)\\
&= \frac{1}{2}\hbar\omega_{\mathbf{q}s} + k_B T \ln\left(1 - e^{-\beta\hbar\omega_{\mathbf{q}s}}\right) && (3)\\
S_{\mathbf{q}s} &= -\left(\frac{\partial F_{\mathbf{q}s}}{\partial T}\right)_v && (4)\\
&= -k_B \ln\left(1 - e^{-\beta\hbar\omega_{\mathbf{q}s}}\right) + k_B \frac{\beta\hbar\omega_{\mathbf{q}s}}{e^{\beta\hbar\omega_{\mathbf{q}s}} - 1} && (5)\\
U_{\mathbf{q}s} &= F_{\mathbf{q}s} + T S_{\mathbf{q}s} && (6)\\
&= \frac{1}{2}\hbar\omega_{\mathbf{q}s} + \frac{\hbar\omega_{\mathbf{q}s}}{e^{\beta\hbar\omega_{\mathbf{q}s}} - 1} && (7)\\
C_{v\,\mathbf{q}s} &= \left(\frac{\partial U_{\mathbf{q}s}}{\partial T}\right)_v && (8)\\
&= k_B e^{-\beta\hbar\omega_{\mathbf{q}s}} \left(\frac{\beta\hbar\omega_{\mathbf{q}s}}{1 - e^{-\beta\hbar\omega_{\mathbf{q}s}}}\right)^2 && (9)
\end{aligned}$$

The vibrational parts of the thermodynamic quantities themselves are then obtained by summing the contributions from all modes, at all wave vectors. Taking the Helmholtz free energy as an example

$$F_{\mathrm{vib}} = \sum_{\mathbf{q}} \sum_{s} F_{\mathbf{q}s} \tag{10}$$

For comparison with classical simulation methods (Monte Carlo, molecular dynamics) it may be convenient to calculate the free energy and dependent quantities in the classical ($k_B T \gg \hbar\omega$) limit. In this case we have:

$$\begin{aligned}
Z^{\mathrm{class}}_{\mathbf{q}s} &= \frac{k_B T}{\hbar\omega_{\mathbf{q}s}} && (11)\\
F^{\mathrm{class}}_{\mathbf{q}s} &= k_B T \ln \beta\hbar\omega_{\mathbf{q}s} && (12)\\
S^{\mathrm{class}}_{\mathbf{q}s} &= k_B \left(1 - \ln \beta\hbar\omega_{\mathbf{q}s}\right) && (13)\\
U^{\mathrm{class}}_{\mathbf{q}s} &= k_B T && (14)\\
C^{\mathrm{class}}_{v\ \ \mathbf{q}s} &= k_B && (15)\\
\frac{\partial F^{\mathrm{class}}_{\mathbf{q}s}}{\partial \mathcal{E}} &= \frac{k_B T}{2\omega^2_{\mathbf{q}s}} \frac{\partial \omega^2_{\mathbf{q}s}}{\partial \mathcal{E}} && (16)
\end{aligned}$$

Because the system under consideration is a periodic crystal of infinite extent the $\mathbf{q}$ summation becomes an averaged integration over the first Brillouin zone. This can be approximated as an averaged sum over any set of reciprocal lattice vectors $\mathbf{q}$ in the first Brillouin zone; the quality of the approximation will be determined by the distribution and density of the vectors selected. For modes in which such a summation is performed, the program's execution time will scale roughly as the number of vectors used, since evaluation of the dynamical properties is the most time consuming task, and few quantities can profitably be retained between vectors. This program uses a mesh of M^3 points uniformly distributed through the first Brillouin zone according to the scheme of Chadi and Cohen, where M is specified at run time. The size and symmetry of the unit cell, temperature and accuracy required are factors which will determine the value of M used. In general the only reliable way of making this decision will be to make calculations in the region of interest with a variety of mesh densities and examine the convergence of properties of interest with increasing M.

1.1 Grüneisen parameters

The Grüneisen parameter(s) characterise the change in the frequencies $\omega_{\mathbf{q}s}$ with applied strain. Various different ones can be used: in general a mode Grüneisen parameter for a given strain $\mathcal{E}_i$ is defined

$$\gamma^j_{\mathbf{q}s} = -\frac{\partial \ln \omega_{\mathbf{q}s}}{\partial \mathcal{E}_j} \tag{17}$$

$$= -\frac{1}{\omega_{\mathbf{q}s}}\frac{\partial \omega_{\mathbf{q}s}}{\partial \mathcal{E}_j} \tag{18}$$

$$= -\frac{1}{2\lambda_{\mathbf{q}s}}\frac{\partial \lambda_{\mathbf{q}s}}{\partial \mathcal{E}_j} \tag{19}$$

where $\lambda_{\mathbf{q}s} = \omega^2_{\mathbf{q}s}$ as in section V.A of I, and the partial derivatives are taken at constant temperature, and in such a way that all the other strains are unchanged. The corresponding thermodynamic Grüneisen parameter is then

$$\gamma^j = \frac{\sum_{\mathbf{q}s} C_{v\,\mathbf{q}s}\,\gamma^j_{\mathbf{q}s}}{\sum_{\mathbf{q}s} C_{v\,\mathbf{q}s}} \tag{20}$$

$$= \frac{1}{C_v}\sum_{\mathbf{q}s} C_{v\,\mathbf{q}s}\,\gamma^j_{\mathbf{q}s} \tag{21}$$

where $C_{v\,\mathbf{q}s}$ is the mode contribution to the constant strain heat capacity. By differentiation of (4) and comparison with (8) it can also be seen that

$$\gamma^j = \frac{1}{C_v}\frac{\partial S}{\partial \mathcal{E}_j} \tag{22}$$

The quantities of most use are the first three γ^λ (the macroscopic thermodynamic Grüneisen parameters corresponding to ϵ_1, ϵ_2 and ϵ_3), and γ, the constant pressure thermodynamic Grüneisen parameter, which is a γ as defined above corresponding to a strain $\mathcal{E} = \ln V$, thus

$$\gamma_{\mathbf{q}s} = -\left(\frac{\partial \ln \omega_{\mathbf{q}s}}{\partial \ln V}\right)_P \tag{23}$$

$$\gamma = \frac{V}{C_v}\frac{\partial S}{\partial V} \tag{24}$$

This γ can also be written

$$\gamma = \frac{V\alpha K_T}{C_v} \tag{25}$$

where α is thermal expansion and K_T is bulk modulus

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \tag{26}$$

$$K_T = -V\left(\frac{\partial P}{\partial V}\right)_T \tag{27}$$

For the special case of a cubic crystal $\gamma^1 = \gamma^2 = \gamma^3 = \gamma$.

2 Expanded derivation of the shell model lattice dynamics

Considering the static energy Ψ_{stat} of the whole lattice, the equations of motion for particle i in the unit cell labelled $\mathbf{x}'$ are given by

$$-m_i \ddot{r}^{\alpha}_{i\mathbf{x}'} = \sum_{j\beta\mathbf{x}''} B^{\alpha\beta}_{i\mathbf{x}'j\mathbf{x}''} u^{\beta}_{j\mathbf{x}''} \tag{28}$$

where

$$B^{\alpha\beta}_{i\mathbf{x}'j\mathbf{x}''} = \frac{\partial^2 \Psi_{\text{stat}}}{\partial u^{\alpha}_{i\mathbf{x}'} \partial u^{\beta}_{j\mathbf{x}''}} = \left(\frac{\partial^2}{\partial u^{\alpha}_{i\mathbf{x}'} \partial u^{\beta}_{j\mathbf{x}''}}\right) \frac{1}{2} \sum_{k\mathbf{y}'l\mathbf{y}''}{}' \phi_{kl}(r_{k\mathbf{y}'l\mathbf{y}''}) \tag{29}$$

Assuming[1] the following plane wave form for the solutions to (28)

$$u^{\alpha}_{i\mathbf{x}} = \frac{1}{\sqrt{m_i}} \sum_{\mathbf{q}s} A_{\mathbf{q}s} f^{\alpha}_{\mathbf{q}si} e^{i[\mathbf{q}.\mathbf{x} + \omega_{\mathbf{q}s} t]} \tag{30}$$

then substitution into (28) gives

$$\omega^2_{\mathbf{q}s} f^{\alpha}_{\mathbf{q}si} = \sum_{j\beta} \frac{1}{\sqrt{m_i m_j}} B^{\alpha\beta}_{ij}(\mathbf{q}) f^{\beta}_{\mathbf{q}sj} \tag{31}$$

where

$$\begin{aligned} B^{\alpha\beta}_{ij}(\mathbf{q}) &= \sum_{\mathbf{x}''} e^{i\mathbf{q}.(\mathbf{x}''-\mathbf{x}')} B^{\alpha\beta}_{i\mathbf{x}'j\mathbf{x}''} \\ &= \sum_{\mathbf{x}} e^{i\mathbf{q}.\mathbf{x}} B^{\alpha\beta}_{i\mathbf{0}j\mathbf{x}} \end{aligned} \tag{32}$$

[1] In the following equations, as elsewhere in the paper, i signifies $\sqrt{-1}$ when it appears other than as a subscript.

The last equivalence follows from the translational invariance of the lattice. For convenience we define, in the usual way, the *dynamical matrix* $D_{ij}^{\alpha\beta}(\mathbf{q})$ to be

$$D_{ij}^{\alpha\beta}(\mathbf{q}) = \frac{1}{\sqrt{m_i m_j}} B_{ij}^{\alpha\beta}(\mathbf{q}) \tag{33}$$

From (30), (31) and (33) it can be seen that the $3n$ eigenvalues and eigenvectors of $D_{ij}^{\alpha\beta}(\mathbf{q})$ are the $\omega_{\mathbf{q}s}^2$ and $f_{\mathbf{q}si}^{\alpha}$ respectively, where $\omega_{\mathbf{q}s}$ is the frequency of the vibrational mode labelled s with wave vector $\mathbf{q}$ and $f_{\mathbf{q}sj}^{\alpha}\exp(i[\mathbf{q}.\mathbf{x} + \omega_{\mathbf{q}s}t])$ gives the corresponding displacement for that mode in direction α of particle type j in cell $\mathbf{x}$ at time t.

This procedure must be modified if some of the particles are shells, since if some $m_i = 0$ then clearly the dynamical matrix cannot be evaluated using (33). Instead the core and shell parts may be treated separately in (28) [2] leading to an equation which can be conveniently written

$$\begin{aligned} -m_C\ddot{r}_C &= B_{CC}r_C + B_{CS}r_S \\ 0 &= B_{SC}r_C + B_{SS}r_S \end{aligned} \tag{34}$$

where B_{CS} is a matrix containing those parts of $B_{i\mathbf{x}'j\mathbf{x}''}^{\alpha\beta}$ for which i is of type core and j is of type shell, and a similar notation operates for B_{CC}, B_{SS}, m_C, m_S, r_C and r_S. The dynamical matrix can then be written as the more general expression

$$D_{ij}^{\alpha\beta}(\mathbf{q}) = \frac{1}{\sqrt{m_i m_j}} \left[B_{CC} - B_{CS}B_{SS}^{-1}B_{SC}\right]_{ij}^{\alpha\beta}(\mathbf{q}) \tag{35}$$

the i and j now referring only to core particles. Once this *effective core-core dynamical matrix* has been evaluated it can be treated as would a dynamical matrix for a cores-only system, and no further consideration of the shells is necessary.

3 Expressions for pair potentials

The Coulomb potential is defined in the usual way

$$\phi_{ij[\mathrm{Coul}]}(r_{ij}) = \frac{z_i z_j}{4\pi\varepsilon_0}\frac{1}{r_{ij}} \tag{36}$$

In Shell the short ranged potential may be specified as any sum of exponential, inverse power, and offset spring terms

$$\phi_{\mathrm{short}}(r) \equiv V_{\mathrm{short}}^0(r) = \sum_{l=1}^{N_{\mathrm{exp}}} A_l e^{-r/R_l} + \sum_{l=1}^{N_{\mathrm{inv}}} C_l r^{-n_l} + \sum_{l=1}^{N_{\mathrm{spr}}} \frac{k_l}{2}(r - s_l)^2 \tag{37}$$

where the ubiquitous ij subscripts have been dropped for clarity.

The exponential and inverse power terms will typically be used to form a Buckingham potential. The spring term with an offset s_l of zero is appropriate for the shell-core springs of the shell model, and with a non-zero offset it can be used (in conjunction with other potentials) to simulate a three-body potential. The user must specify minimum and maximum cutoffs along with the coefficients for each terms.

It would of course be easy to add different terms.

Expressions for the functions V_{ij} are then easily found using (I.46) (I.47) and (37):

$$V^1_{\mathrm{short}}(r) = -\sum_{l=1}^{N_{\mathrm{exp}}} A_l \frac{1}{rR_l} e^{-r/R_l} - \sum_{l=1}^{N_{\mathrm{inv}}} C_l n_l r^{-n_l-2} - \sum_{l=1}^{N_{\mathrm{spr}}} k_l \left(1 - \frac{s_l}{r}\right) \tag{38}$$

$$V^2_{\mathrm{short}}(r) = \sum_{l=1}^{N_{\mathrm{exp}}} A_l \left(\frac{1}{r^2 R_l^2} + \frac{1}{r^3 R_l}\right) e^{-r/R_l} + \sum_{l=1}^{N_{\mathrm{inv}}} C_l n_l (n_l + 2) r^{-n_l-4} + \sum_{l=1}^{N_{\mathrm{spr}}} k_l \frac{s_l}{r^3} \tag{39}$$

$$V^3_{\mathrm{short}}(r) = -\sum_{l=1}^{N_{\mathrm{exp}}} A_l \left(\frac{3}{r^5 R_l} + \frac{3}{r^4 R_l^2} + \frac{1}{r^3 R_l^3}\right) e^{-r/R_l} - \sum_{l=1}^{N_{\mathrm{inv}}} C_l n_l (n_l + 2)(n_l + 4) r^{-n_l-6} - \sum_{l=1}^{N_{\mathrm{spr}}} 3k_l \frac{s_l}{r^5} \tag{40}$$

References

[1] Taylor M B, Barrera G D, Allan N L and Barron T H K, Phys. Rev. B *56*, 14380 (1997)

[2] Born M and Huang K, *Dynamical Theory of Crystal Lattices*, Oxford University Press (1954)