Lattice vibrations in the harmonic approximation

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Abstract We present some theoretical results on the lattice vibrations that are necessary for a concise derivation of the Debye-Waller factor in the harmonic approximation. First we obtain an expression for displacement of an atom in a crystal lattice from its equilibrium position. Then we show that an atomic displacement has the Gaussian distribution. Finally, we obtain the computational formula for the Debye-Waller factor in the Debye model.

Keywords Debye-Waller factor · Normal modes · Gaussian distribution · Debye model · Ferromagnetic metals

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1 Introduction

Neutron scattering experiment is used for studying the magnetic short-range order in metals, which is described by the spin-density correlator. The contribution of the electron subsystem to the spin correlator at finite temperatures was calculated in the dynamic spin-fluctuation theory [1] and compared with experiment in our paper [2]. Lattice vibrations lead to the correction coefficient to the spin-density correlator. The coefficient that corresponds to the elastic phonon scattering is called the Debye-Waller factor (DWF). Numerical results and discussion of the DWF in metals are given in our paper [3]. In particular, we showed that an estimate of the DWF in the harmonic approximation can be sufficient for calculating the correction to local magnetic characteristics.
Usually the DWF is obtained by a lengthy calculation of the mean-square displacement (see, e.g., [4]), which is valid both in the harmonic and anharmonic approximations. In the paper [3], we give a simple derivation of the same expression for the DWF in the harmonic approximation. Our derivation is based on the formula for canonical average of exponentials of operators linear in the atomic displacements, which was obtained by Mermin [5]. Here we present some theoretical details on the lattice vibrations in the harmonic approximation that are used in our paper [3].

The paper is structured as follows. In Sec. 2 we obtain an expression for displacement of an atom in a crystal lattice from its equilibrium position. We start with the classical mechanics treatment of the normal modes and then show how they are quantized. In Sec. 3 we prove that a normal mode displacement has the Gaussian probability distribution. Following [6], we do this by calculating the displacement characteristic function. However, in [6] the calculation is rather tedious. Application of Mermin’s formula [5] allows us to omit the quantum-statistical treatment of the characteristic function and derive it in one line. In Sec. 4 we introduce the Debye model and give details of its application to the DWF [3] (for calculation of heat capacity in the Debye model, see, e.g., [7, 8]).

2 Normal Modes and Their Quantization

In the harmonic approximation, the classical Hamiltonian of a three-dimensional crystal lattice is (see, e.g., [5])

\[
H = \sum_j p_j^2 - \frac{1}{2M} \sum_{jj'} u_j \cdot D_{jj'} u_{j'},
\]

(1)

where \(M\) is the mass of an atom, \(p_j\) is the momentum of the \(j\)th atom, \(u_j\) is the displacement of the \(j\)th atom from its equilibrium position, and \(D_{jj'}\) is the \(3 \times 3\)-matrix of the form

\[
D_{jj'} = \left. \frac{\partial^2 U}{\partial u_j \partial u_{j'}} \right|_{u=0}.
\]

(2)

Here \(U = U(u_1, \ldots, u_N)\) is the potential energy, which attains its minimum at the equilibrium \(u = 0\). From the Hamiltonian system,

\[
\frac{dp_j}{dt} = -\frac{\partial H}{\partial u_j}, \quad \frac{du_j}{dt} = \frac{\partial H}{\partial p_j},
\]

we obtain the equation of motion

\[
M \frac{d^2 u_j}{dt^2} = -\sum_{j'} D_{jj'} u_{j'}.
\]

(3)

We seek a particular solution in the form

\[
u_{jq}(t) = Q_q e^{iqR_j - i\omega_q t},
\]

(4)
where $e_q$ is the polarization vector, $Q_q$ is the (complex) amplitude and $\omega_q$ is the frequency of the oscillation. The wave determined by (3) is called the normal mode. Substituting expression (4) in (3), we obtain
\[
M\omega_q^2 e_q = \sum_{j'} D_{jj'} e_q e^{-i\mathbf{q}\cdot\mathbf{R}_{j'-j}}.
\]
(5)

Due to homogeneity of the crystal, the matrix $D_{jj'}$ depends only on the distance between the sites: $D_{jj'} = D_{j-j'}$. Hence its Fourier transform is a diagonal matrix with the elements
\[
D_q = \sum_{j} D_{jj} e^{-i\mathbf{q}\cdot\mathbf{R}_{j-j'}} = \sum_{j'} D_{j-j'} e^{-i\mathbf{q}\cdot\mathbf{R}_{j-j'}}
\]
at the diagonal. Substituting (6) in (5), we see that $e_q$ is an eigenvector of $D_q$:
\[
D_q e_q = M\omega_q^2 e_q.
\]
(6)

Since the matrix (2) is symmetric, its eigenvalues are real and its eigenvectors $e_{qi}, i = 1, 2, 3$, can be chosen such that they form an orthonormal basis in the three-dimensional space,
\[
D_q e_{qi} = M\omega_q^2 e_{qi}, \quad i = 1, 2, 3.
\]
(7)

We can also choose $e_{qi}$ such that $e_{-qi} = e_{qi}$. Each of the vectors $e_{qi}$ determines the direction of the normal mode oscillation with the frequency $\omega_{qi}$. The general solution to equation (3) is
\[
u_j(t) = N^{-1/2} \sum_{qi} Q_{qi} e_{qi} e^{i\mathbf{q}\cdot\mathbf{R}_j - i\omega_{qi} t},
\]
(8)

where the summation over $\mathbf{q}$ is carried out over the Brillouin zone. Then the momentum is written as
\[
p_j(t) = N^{-1/2} \sum_{qi} P_{qi} e_{qi} e^{i\mathbf{q}\cdot\mathbf{R}_j - i\omega_{qi} t}.
\]
(9)

Since the displacement (8) and momentum (9) are real quantities, the Fourier coefficients $P_{qi}$ and $Q_{qi}$ satisfy $P_{-qi} = P_{qi}^*$ and $Q_{-qi} = Q_{qi}^*$.

We use $P_{qi}$ and $Q_{qi}$ as new coordinates, in which the system becomes an ensemble of independent oscillators. Substituting expressions (5) and (9) at $t = 0$ in the Hamiltonian (1) and using the identity
\[
\sum_j e^{i(\mathbf{q}+\mathbf{q'})\cdot\mathbf{R}_j} = N\delta_{\mathbf{q}',-\mathbf{q}},
\]
(10)

we write the first term as
\[
H_0 = \frac{1}{2M} \sum_{qi'q} P_{qi} P_{-q'q'} e_{qi} \cdot e_{-q'i'}.
\]
(11)

Similarly, using (9) and (10), we develop the second term of (1) to
\[
H_1 = \frac{1}{2} \sum_{qi'q} Q_{qi} Q_{-q'q'} e_{qi} \cdot D_q e_{-q'i'}.
\]
Recalling that $e_{qi}$ is an eigenvector of the matrix $D_q$ and applying equation (7), we obtain

$$H_1 = \frac{1}{2} \sum_{q_i,q_i'} M \omega^2_{qi} Q_{qi} Q_{-qi'} e_{qi} \cdot e_{-qi'}.
\tag{12}$$

Finally, applying $e_{qi} \cdot e_{-qi'} = e_{qi} \cdot e_{qi'} = \delta_{i,i'}$ to (11) and (12), we write the Hamiltonian (11) as

$$H = H_0 + H_1 = \sum_{q_i} \left( \frac{1}{2M} |P_{qi}|^2 + \frac{1}{2} M \omega^2_{qi} |Q_{qi}|^2 \right).
\tag{13}$$

We now replace $P_{qi}$ and $Q_{qi}$ by their usual quantum mechanical operators $\hat{P}_{qi}$ and $\hat{Q}_{qi}$ to obtain the operator form of the Hamiltonian. The creation and annihilation operators for the $q_i$-th mode are defined by

$$b_+^{qi} = (2M\hbar\omega_{qi})^{-1/2} \left( M\omega_{qi} \hat{Q}_{-qi} - i \hat{P}_{qi} \right),
\quad b_0^{qi} = (2M\hbar\omega_{qi})^{-1/2} \left( M\omega_{qi} \hat{Q}_{qi} + i \hat{P}_{-qi} \right).
\tag{14}$$

These quantized normal modes are the boson-type quasi-particles called *phonons*. Taking into account the commutation relations

$$[\hat{Q}_{qi}, \hat{Q}_{qi'}] = [\hat{P}_{qi}, \hat{P}_{qi'}] = 0, \quad [\hat{P}_{qi}, \hat{Q}_{qi'}] = \delta_{q,q'} \delta_{i,i'},$$

we write the Hamiltonian (13) in the second-quantized form:

$$H = \sum_{q_i} \hbar \omega_{qi} \left( b_+^{qi} b_0^{qi} + \frac{1}{2} \right).
\tag{15}$$

Next, we obtain the operator form of the displacement $\hat{u}_j$. Expressing $\hat{Q}_{qi}$ from (14),

$$\hat{Q}_{qi} = \left( \frac{\hbar}{2M\omega_{qi}} \right)^{1/2} \left( b_0^{qi} + b_+^{qi} \right),$$

and substituting the latter in (15), we obtain

$$\hat{u}_j = \left( \frac{\hbar}{2MN} \right)^{1/2} \sum_{q_i} \omega_{qi}^{-1/2} e_{qi} \left( b_0^{qi} + b_+^{qi} \right) e_{qiR_j}.$$

Making use of

$$\sum_{q_i} \omega_{qi}^{-1/2} e_{qi} b_+^{qi}\ e_{qiR_j} = \sum_{q_i} \omega_{qi}^{-1/2} e_{qi} b_0^{qi}\ e_{-qiR_j},$$

we write the displacement operator in the second-quantized form:

$$\hat{u}_j = \left( \frac{\hbar}{2MN} \right)^{1/2} \sum_s \omega_s^{-1/2} e_s \left( b_s e_{qiR_j} + b_+^s e_{-qiR_j} \right),
\tag{16}$$

where $s = (q, i)$.
3 Gaussian Distribution of Normal Modes

We show that the atomic displacement (16) has the Gaussian distribution. We start with the canonical average

\[
\langle f(\hat{u}_j^\alpha) \rangle = \frac{1}{Z} \text{Tr} \left( f(\hat{u}_j^\alpha) e^{-\mathcal{H}/T} \right),
\]

where \( f(\hat{u}_j^\alpha) \) is a function of the displacement \( \hat{u}_j^\alpha \) (hereafter the indices are omitted for brevity), \( Z = \text{Tr} e^{-\mathcal{H}/T} \) is the partition function, \( \mathcal{H} \) is the Hamiltonian of the crystal lattice (15) and \( T \) is temperature (in energy units). Assuming the states \( \psi_\lambda \) to be the eigenfunctions of the Hamiltonian:

\[
\mathcal{H} \psi_\lambda = E_\lambda \psi_\lambda, \quad e^{-\mathcal{H}/T} \psi_\lambda = e^{-E_\lambda/T} \psi_\lambda,
\]

we transform the trace in (17) as

\[
\langle f(\hat{u}) \rangle = \frac{1}{Z} \sum_\lambda e^{-E_\lambda/T} \int f(u) |\psi_\lambda(u)|^2 \, du.
\]

Introducing the probability density function

\[
p(u) = \frac{1}{Z} \sum_\lambda |\psi_\lambda(u)|^2 e^{-E_\lambda/T},
\]

we obtain the integral representation for the canonical average (17):

\[
\langle f(\hat{u}) \rangle = \int f(u) p(u) \, du.
\]

We show that \( p(u) \) is the Gaussian probability density. We prove this by calculating the characteristic function (see, e.g., [9]):

\[
\varphi(x) = \int p(u) e^{iux} \, du,
\]

which is the Fourier transform of \( p(u) \). Hence the probability density function \( p(u) \) is obtained by the inverse Fourier transform of the characteristic function:

\[
p(u) = \frac{1}{2\pi} \int \varphi(x) e^{-ixu} \, dx.
\]

We calculate the characteristic function (19) as follows. Since the integral representation (18) is equivalent to the canonical average (17), we rewrite (19) as

\[
\varphi(x) = \frac{1}{Z} \text{Tr} \left( e^{ix\hat{u}} e^{-\mathcal{H}/T} \right) = \langle e^{ix\hat{u}} \rangle.
\]

Taking expression (16) into account, we write the displacement operator \( \hat{u} \) as

\[
\hat{u} = \sum_s (\gamma_s b_s + \gamma_s^* b_s^\dagger),
\]

where we introduced the short notation

\[
\gamma_s = \left( \frac{\hbar}{2MN} \right)^{1/2} \frac{e_s}{\sqrt{\omega_s}} e^{iqR_j}.
\]
The canonical average of the exponential $\langle e^Q \rangle$ with an operator $Q$ linear in $b_s$ and $b_s^\dagger$: $Q = \sum_s (c_s b_s + d_s b_s^\dagger)$ is calculated by the formula [5]

$$\langle e^Q \rangle = \exp \left[ \frac{1}{2} \sum_s c_s d_s \coth \left( \frac{\hbar \omega_s}{2T} \right) \right].$$

(24)

Using expression (22) and formula (24), we write the characteristic function (21) in the form

$$\varphi(x) = e^{-\frac{1}{2} x^2 \sigma^2},$$

where

$$\sigma^2 = \sum_s |\gamma_s|^2 \coth \left( \frac{\hbar \omega_s}{2T} \right).$$

(25)

Using (26), we have

$$\sigma^2 = \frac{\hbar}{2MN} \sum_s \frac{1}{\omega_s} \coth \left( \frac{\hbar \omega_s}{2T} \right).$$

(26)

Substituting (25) in (20), we obtain

$$p(u) = \frac{1}{2\pi} \int e^{-ixu} e^{-\frac{1}{2} x^2 \sigma^2} \, dx.$$

After completing the square, we have

$$p(u) = \frac{1}{2\pi} e^{-\frac{1}{2} u^2 / \sigma^2} \int e^{-\frac{1}{2} (x\sigma - iu/\sigma)^2} \, dx = \frac{1}{\sigma \sqrt{2\pi}} e^{-\frac{1}{2} u^2 / \sigma^2}.$$

The latter is the Gaussian probability density function with the zero mean and mean-square displacement $\langle u^2 \rangle = \sigma^2$ (see, e.g., [9]).

4 The Debye Model

The Gaussian probability distribution of displacement substantially simplifies calculation of the DWF $e^{-2W(\kappa)}$, where

$$2W(\kappa) = \frac{1}{3} \kappa^2 \langle u^2 \rangle.$$

(27)

In the paper [3], we obtain expression (27) directly using the formula (24) in the harmonic approximation, instead of a lengthy calculation of the mean-square atomic displacement valid both in the harmonic and anharmonic approximations (see, e.g., [4]). Taking (26) into account, we write

$$2W(\kappa) = \frac{\hbar \kappa^2}{6MN} \sum_s \frac{1}{\omega_s} \coth \left( \frac{\hbar \omega_s}{2T} \right).$$

(28)

To calculate the sum over frequencies of the normal modes $\omega_s$, we convert it to the integral over the frequencies with the phonon density of states $n(\omega)$ by the formula

$$\sum_s f(\omega_s) = \int f(\omega) n(\omega) \, d\omega,$$

(29)
where \( f(\omega) \) is an arbitrary function. Thus, for calculation in real metals, we need the phonon density of states \( n(\omega) \).

By definition, the phonon density of states is given by

\[
n(\omega) = \frac{dN(\omega)}{d\omega},
\]

(30)

where \( N(\omega) \) is the number of normal modes with phonon frequencies less or equal than \( \omega \). First, we calculate the number of normal modes \( N(q) \) with magnitude of the phonon wavevectors less or equal than \( q \). Since the wavevector \( q \) takes \( N \) discrete values in the Brillouin zone, we have one \( q \) value per \( (2\pi)^3/V \) volume. Then \( N(q) \) is obtained by dividing the volume of the sphere of radius \( q \) by the volume \( (2\pi)^3/V \) and multiplying by three (the number of polarization modes \( i \)):

\[
N(q) = \frac{4\pi q^3 V}{(2\pi)^3}.
\]

(31)

In the Debye model it is assumed that \( \omega = vq \), where \( v \) is the velocity of sound. Substituting \( q = \omega/v \) in (31), we have

\[
N(\omega) = \frac{\omega^3 V}{2\pi^2 v^3}.
\]

Differentiating the latter, we write (30) as

\[
n(\omega) = \frac{3\omega^2 V}{2\pi^2 v^3}.
\]

(32)

Replacing the Brillouin zone by the equal-volume sphere of the Debye radius \( q_D \), we have \( N(q_D) = 3N \). Hence from (31) we obtain \( q_D^3 = 6\pi^2 N/V \). Substitution of the latter in \( v^3 = q_D^3/\omega_D^3 \) gives

\[
v^3 = \frac{V\omega_D^3}{6\pi^2 N},
\]

(33)

where the Debye frequency \( \omega_D \) is the maximum frequency of the normal modes. Substituting (33) in (32), we obtain the final expression for the phonon density of states in the Debye model:

\[
n(\omega) = \frac{9N\omega^2}{\omega_D^3}, \quad 0 \leq \omega \leq \omega_D.
\]

(34)

Now we are in position to calculate the DWF (28). Applying (29) to (28), we write the latter in the form:

\[
2W(\kappa) = \frac{\hbar \kappa^2}{6MN} \int \frac{1}{\omega} \coth \left( \frac{\hbar \omega}{2T} \right) n(\omega) \, d\omega.
\]

(35)

Substituting (34) in (35), we have

\[
2W(\kappa) = \frac{3\hbar \kappa^2}{2M\omega_D} \int_{\omega_D}^{\omega} \coth \left( \frac{\hbar \omega}{2T} \right) \omega \, d\omega.
\]
At high temperatures, using \( \coth x \approx \frac{1}{x} \) for \( x \ll 1 \), we finally obtain

\[
2W(\kappa) = \frac{3\hbar^2\kappa^2}{M} \frac{T}{\Theta_D}, \quad T \gg \Theta_D,
\]

where \( \Theta_D = \hbar\omega_D \) is the Debye temperature.

To conclude, we have presented theoretical results on the lattice vibrations in the harmonic approximation and applied them to the DWF calculation. First, we derived an expression for atomic displacement in a crystal lattice. Next, we proposed a concise method for calculating the characteristic function of atomic displacement. As a consequence, we obtained that atomic displacement has the Gaussian distribution. This fact allows to simplify the derivation of the DWF in the harmonic approximation. Finally, we obtained the computational formula for the DWF in the Debye model. The formula can be used directly for estimating the DWF in metals.

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