Note on Frequency Spectrum of Crystalline Fine Particles

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Frequency distribution function of lattice vibration in crystalline fine particles is calculated as functions of fine particle radius by means of the moment-trace method. An FCC lattice with nearest neighbour central interaction is considered as an example and the 2n-th moment of frequency distribution is expressed as a sum over paths on the lattice connected by the dynamical matrix elements. The presence of surface gives a restriction on the sum over paths. It is shown that the frequency distribution functions constructed with the first five even moments show remarkable tendency for the phonon softening as fine particle radius becomes small.

§ 1. Introduction

In previous two papers,\textsuperscript{1,2} referred to as I and II respectively, we have developed a theory of anharmonic lattice vibration in metallic fine particles on the basis of the self-consistent Einstein model. The theory was applied in I to discuss the size dependence of the melting and superconducting transition temperatures of fine particles, and in II the limitation of high temperature approximation used in I was removed so as to include the low temperature regions with an application to the Mössbauer spectroscopy of metallic fine particles.

The general trend predicted from the theory for the size dependence in the melting temperature, superconducting transition temperature, and Debye-Waller factor deduced from the Mössbauer fraction agrees with the experiments qualitatively, but quantitatively there remain large discrepancies between the theory and experiments. In order that the theory is more quantitative, improvements of the theory are necessary for several directions. Among all, when we have to account for an experiment at very low temperatures such as superconductivity, it is essential to take into account the low-lying phonon excitations, and hence the Einstein model itself becomes inadmissible: One has to consider the frequency distribution of lattice vibrations. Therefore, before scrutinizing the previous theory so as better agreement between the theory and experiments is attained, it would be useful to present a method of calculating the frequency distribution function of lattice vibration in crystalline fine particles.

For an illustrative purpose, we consider in this paper an FCC lattice of finite size with only nearest neighbour interaction via a central force. Using the moment-trace method invented by Montroll,\textsuperscript{3} we examine how the frequency distribution function is changed from the bulk value by the perturbations due to the finiteness
of the lattice or the presence of the surface. Similar problems have been studied by several authors by making use of the computer simulation. For instance, Dickey and Paskin have computed the frequency spectrum of finite FCC lattices with various shapes, and demonstrated the presence of the surface edge modes by comparing the frequency spectra for different finite crystals. Kristensen, Jensen and Cotterill have performed the computer experiment similar to Dickey and Paskin's but for larger size of lattice. Maradudin, Wallis, Mills and Ballard have also examined the vibrational edge mode in a finite lattice. The aim of this paper is, supplementing the informations gained from the computer experiment approaches, to present a theoretical method of calculating the frequency spectrum of crystalline fine particles within the harmonic approximation, and further to enable us to incorporate the present results into a more general theory of anharmonic lattice vibration in metallic fine particles in our future works.

The organization of this paper is as follows. In the next section a brief account of the model and the moment-trace method is given. In § 3 the effect of surface is carefully examined and the moments of frequency distribution for a fine particle are given up to the first five even orders. Then the numerical results for the moments and the frequency distribution functions for various surface to volume ratios are shown in § 4. The final section is devoted to discussion and a future plan of generalization.

§ 2. Model and formulation

We consider a spherical particle with a radius $R$, composed of atoms forming an FCC lattice. Let $N$ be the total number of atoms included in the sphere and $2a$ be the linear dimension of the unit cell cube. We denote the dynamical matrix by

$$ D = [D_{\alpha\beta}(l, l')] $$

with

$$ D_{\alpha\beta}(l, l') = \begin{cases} -\phi_{\alpha\beta}(l-l') & \text{for } l \neq l', \\ \sum_{l''} \phi_{\alpha\beta}(l-l'') & \text{for } l = l', \end{cases} $$

where $\alpha = x, y, z$ is the cartesian component and $l$ the site index vector of the $l$-th atom with three integer components $\{l_\alpha\}$. If we assume a central force acting only between the nearest neighbour atoms, it is easily verified that the non-zero $\phi_{x\beta}(l)$ are

$$ \phi_{xx}(l) = \gamma $$

$$ \phi_{xy}(l) = \phi_{yx}(l) = \begin{cases} \gamma & \text{for } l = (\pm 1, 0, \pm 1), \\ -\gamma & \text{for } l = (1, 1, 0), (-1, -1, 0), \end{cases} $$

and similar ones obtained by making cyclic permutation $(x \rightarrow y \rightarrow z)$. From the
Note on Frequency Spectrum of Crystalline Fine Particles

(2) it follows that

\[ D_{\alpha\beta}(l, l) = \begin{cases} 0 & \text{for } \alpha \neq \beta, \\ 8l^3 & \text{for } \alpha = \beta. \end{cases} \tag{4} \]

The frequencies of the normal modes \( \nu_i(\lambda = 1, 2, \ldots 3N) \) are derived from the 3N eigenvalues of the dynamical matrix \( D \).

Now, following Montroll,\textsuperscript{3} we try to approximate the frequency distribution function \( G(\nu) \) by a polynomial function of \( \nu \):

\[ G(\nu) = \sum \alpha \nu^2 \alpha n. \]

By definition, \( G(\nu) \) should satisfy the sum rule

\[ \int_0^{\nu_L} G(\nu) d\nu = 3N \tag{5} \]

with the largest frequency \( \nu_L \). It is convenient to introduce a normalized frequency \( x = \nu / \nu_L \) and a normalized frequency distribution function

\[ g(x) = \nu_L G(\nu_L x) / 3N \tag{6} \]

such that

\[ g(\nu / \nu_L) = \sum_{n=0}^{k} \alpha_2n (\nu / \nu_L)^{2n}, \]

\[ \int_0^1 g(x) dx = 1. \tag{7} \]

The coefficients \( \{a_{2n}\} \) of the polynomial in Eq. (7) can be determined in such a way that \( g(x) \) has the correct even moments:

\[ \int_0^1 g(x) x^{2k} dx = \mu_{2k}. \tag{8} \]

The formula connecting \( \{a_{2n}\} \) and \( \{\mu_{2j}\} \) has been already derived by Montroll as

\[ a_{2n} = \frac{(2n + 2k + 1)!}{2^{k}(n + k)! (k - n)! (2n)!} \sum_{j=1}^{k} (-1)^{n+j} (2j + 2k + 1)! \mu_{2j} \frac{(-1)^{n+j}(2j + 2k + 1)! \mu_{2j}}{\mu_{2j} (j + k)! (k - j)! [2(n + j) + 1] (2j)!}. \tag{9} \]

As is well known, the \( 2j \)-th moment \( \mu_{2j} \) is related with the trace of the \( j \)-th power of the dynamical matrix \( D \):

\[ \mu_{2j} = \text{Tr} D^j / 3N (2\pi \nu_L)^{2j}. \tag{10} \]

When the dynamical matrix \( D \) has the translational symmetry of an infinite crystal, the evaluation of the trace in Eq. (10) can be performed rather easily in the wave vector space by diagonalizing \( D \). Indeed, Montroll and his co-worker have computed the moments of the frequency distribution in this way up to \( j = 7 \) for SC.
lattice\textsuperscript{7} and BCC lattice\textsuperscript{8} with the second neighbour central interactions. More recently Isenberg has used a new technique of utilizing computer to calculate the even moments for FCC lattice up to \( j=34,\textsuperscript{9} \) For finite crystals such as fine particles, however, the evaluation of the trace in the wave vector space is not easy because of the lack of the translational invariance. In the present paper, therefore, we carry out the operation of trace in the coordinate space, expressing the moments as sum over all possible paths on the lattice connected by the dynamical matrix elements.

As a check of our procedure of the trace calculation in the coordinate space, we re-calculate the moments for FCC lattice with the translational symmetry by this method. For instance,

\[
\text{Tr } \mathbf{D} = \sum_{a} \sum_{f} D_{aa}(l, l) = 3N \times 8\gamma
\]

and

\[
\text{Tr } \mathbf{D}^2 = \sum_{a} \sum_{f'} \sum_{f''} D_{aa}(l, l') D_{aa}(l', l'')
\]

\[
= 3N[(8\gamma)^2 + 8\gamma^2 + 2 \times 4\gamma^2] = 3N \times 80\gamma^4
\]

follow immediately from the definitions (3) and (4). Similar elementary and straightforward calculation yields the next few traces of higher power of \( \mathbf{D} \): The results are summarized as

\[
\begin{align*}
\text{Tr } \mathbf{D} &= 3N \times 8\gamma, \\
\text{Tr } \mathbf{D}^2 &= 3N \times 80\gamma^2, \\
\text{Tr } \mathbf{D}^3 &= 3N \times 912\gamma^4, \\
\text{Tr } \mathbf{D}^4 &= 3N \times 11248\gamma^6, \\
\text{Tr } \mathbf{D}^5 &= 3N \times 145568\gamma^8.
\end{align*}
\]

These results are in complete agreement with those of Montroll for SC lattice\textsuperscript{7} obtained by deleting the nearest neighbour interactions. The factor \( N \) in (11) comes from the fact that the sum over initial (and final) sites is equivalent to the multiplication by \( N \) because of the translational symmetry. This is not the case for a finite lattice, the diagonal elements of \( \mathbf{D}^f \) being dependent of site positions. Such surface effect will be considered in the next section.

In the following, we shall content ourselves with a rough approximation for the normalized frequency distribution function, using a small
number of even moments. The number of terms \( k \) in the polynomial function (7) is chosen as 5, because it is shown that this is the smallest number of terms which can realize the main characteristic feature of the frequency distribution function. For reference, we compare in Fig. 1 the normalized frequency distribution function of bulk FCC lattice constructed with five even moments and that obtained by Isenberg\(^9\) with 22 even moments. It should be noticed, therefore, that the arguments which follow in the remainder will be of qualitative nature to the extent as demonstrated in Fig. 1.

§ 3. Surface effect

As stated in § 2, when we evaluate the trace of \( D' \) in the lattice space, the presence of surface imposes a restriction on the summation: Some of the paths permitted interior may be prohibited on and near the surface. This effect causes the reduction in the values of moments of frequency distribution for fine particles. In addition, there is another surface effect originated from anharmonicity. Namely it is shown theoretically and experimentally that the force constants acting on the surface atoms are effectively weakened.\(^10\) Therefore when we take into account this effect later, it is assumed that the force constant parameter \( \gamma \) is reduced by a factor \( \lambda \) for the atoms on and near the surface:

\[
\gamma' = \lambda \gamma. \tag{12}
\]

Now, if we examine carefully the diagonal element of \( [D']_{aa} \) for \( j \leq 5 \), it is found that the surface effects appear only when the site \( l \) is either on the surface or in the first layer. In another word, all the atoms occupying the lattice points of the second layer and inside may be regarded as 'bulk atoms' which make contributions to the moments same as the atoms in an infinite crystal. Thus we can discriminate the contributions to the trace

\[
\sum_{\alpha} \sum_{\beta} [D']_{\alpha\beta}
\]

according as the position of the site \( l \) is on the surface, in the first layer or interior. The number of the lattice points belonging to the above three classes can be readily estimated. For simplicity we assume that the surface is the (001) plane (the \( xyz \)-plane). Since the volume of the unit cell cube is \( 8a^3 \) in which four atoms are included, the atomic volume is \( 2a^3 \). Hence the total number of atoms is

\[
N = (4\pi R^3/3) \left( 2a^3 \right)^{-1}. \tag{13}
\]

On the surface, there are two atoms in a square of area \( 4a^2 \), and hence the surface area per atom is \( 2a^2 \). Therefore the number of surface atoms is given by

\[
(4\pi R^3) \left( 2a^2 \right)^{-1} = N(3a/R). \tag{14}
\]
Table I. Diagonal element of $[D^j]$ for $j \leq 5$ and three different site positions.

<table>
<thead>
<tr>
<th>class of position</th>
<th>surface</th>
<th>first layer</th>
<th>interior</th>
</tr>
</thead>
<tbody>
<tr>
<td>number of atoms</td>
<td>$N(3a/R)$</td>
<td>$N(3a/R)$</td>
<td>$N(1-6a/R)$</td>
</tr>
<tr>
<td>$\sum [D^j]_{sym}$</td>
<td>$16\gamma$</td>
<td>$24\gamma$</td>
<td>$24\gamma$</td>
</tr>
<tr>
<td>$\sum [D^j]_{asym}$</td>
<td>$120\gamma^2$</td>
<td>$240\gamma^2$</td>
<td>$240\gamma^2$</td>
</tr>
<tr>
<td>$\sum [D^j]_{asym}$</td>
<td>$1096\gamma^3$</td>
<td>$2736\gamma^3$</td>
<td>$2736\gamma^3$</td>
</tr>
<tr>
<td>$\sum [D^j]_{asym}$</td>
<td>$11200\gamma^4$</td>
<td>$33640\gamma^4$</td>
<td>$33744\gamma^4$</td>
</tr>
<tr>
<td>$\sum [D^j]_{asym}$</td>
<td>$122512\gamma^5$</td>
<td>$432768\gamma^5$</td>
<td>$436704\gamma^5$</td>
</tr>
</tbody>
</table>

We can safely assume that the number of atoms in the first layer is also given by (13). Then the total number of interior atoms becomes

$$N - 2 \times N(3a/R) = N(1 - 6a/R).$$  \hspace{1cm} (15)

We are now in a position to study the surface correction to the trace of $D^j$ obtained in (11). This is a little tedious but straightforward task and it will be unnecessary to describe the detail of counting the number of paths perturbed by the presence of surface. Instead, we show only the final results which are summarized in Table I.

The trace of $D^j$ is obtained by adding the corresponding row in this Table multiplied by the number of atoms in each class. Thus we have

\[
\begin{align*}
\text{Tr } D &= 3N \times 8\gamma[1 - (a/R)], \\
\text{Tr } D' &= 3N \times 80\gamma^2[1 - (3/2)(a/R)], \\
\text{Tr } D'' &= 3N \times 912\gamma^3[1 - (205/114)(a/R)], \\
\text{Tr } D''' &= 3N \times 11248\gamma^4[1 - (2831/1406)(a/R)], \\
\text{Tr } D'''' &= 3N \times 145568\gamma^5[1 - (19883/9098)(a/R)].
\end{align*}
\]  \hspace{1cm} (16)

To include the effect of anharmonicity, we adopt a crude approximation such that all the force constant parameters $\gamma$'s in the surface and first layer columns of Table I are replaced by $\gamma' = \lambda \gamma$. The traces thus derived are related to the moments of frequency distribution through Eq. (10), and upon noting that the largest frequency of the FCC lattice with nearest neighbour central interaction is given by

$$\left(2\pi\nu_L\right)^4 = 16\gamma,$$  \hspace{1cm} (17)

we obtain from (10) and Table I with the above inclusion of anharmonicity

$$\mu_b = 1,$$

$$\mu_2 = \tau[1 - (6 - 5\lambda)(a/R)].$$
\[ \mu_1 = \frac{5}{4} \tau^2 \left[ 1 - \frac{6 - 9 \lambda^2}{2} \left( \frac{a}{R} \right) \right], \]
\[ \mu_6 = \frac{57}{32} \tau^4 \left[ 1 - \frac{6 - 479 \lambda^2}{114} \left( \frac{a}{R} \right) \right], \]
\[ \mu_8 = \frac{703}{256} \tau^6 \left[ 1 - \frac{6 - 5605 \lambda^2}{1406} \left( \frac{a}{R} \right) \right], \]
\[ \mu_{20} = \frac{4549}{1024} \tau^{20} \left[ 1 - \frac{6 - 34705 \lambda^2}{9098} \left( \frac{a}{R} \right) \right] \]

with
\[ \tau = \frac{8 \rho}{(2 \pi \nu L)^2} = 1/2. \] (18)

It is readily checked that the numerical values of \( \mu_j \)'s in the limit of \( R \to \infty \) coincide with those listed in Table I of Isenberg's paper.\(^9\)

So far we have assumed that the surface is always (001) plane. Actually the surface corrections depend slightly on the directions of surface planes, and it is necessary to take average of the directional dependence for a more accurate calculation. However we shall leave such a sophistication of the theory to our future publication.

\section*{§ 4. Numerical results}

On the basis of the formulation given in the preceding two sections, we present here the numerical results for the normalized even moments and the normalized frequency distribution functions of crystalline fine particles as functions of particle size.

To begin with, we first rewrite the even moments derived in (18) in a compact form as
\[ \mu_{2n} = \mu_{2n}^b \left[ 1 - C_n \left( \frac{a}{R} \right) \right] \text{ for } \lambda = 1 \] (19)
or
\[ \mu_{2n} = \mu_{2n}^b \left[ 1 - (6 - B_n \lambda^n) \left( \frac{a}{R} \right) \right] \text{ for } \lambda < 1. \] (20)

\( \mu_{2n} \) is the 2n-th moment of frequency distribution for bulk crystal. The coefficients \( C_n \) and \( B_n \) are plotted as functions of \( n \) in Figs. 2 and 3 respectively. Both \( C_n \) and \( B_n \) are quite smooth functions of \( n \) and we are tempted to extrapolate them into the range \( n \geq 6 \). For instance, from Fig. 3, \( \mu_{12} \) and \( \mu_{14} \) can be estimated as
\[ \mu_{12} = \mu_{12}^b \left[ 1 - (6 - 3.66 \lambda^6) \left( \frac{a}{R} \right) \right] \] (21)
and
\[ \mu_{14} = \mu_{14}^b \left[ 1 - (6 - 3.55 \lambda^7) \left( \frac{a}{R} \right) \right]. \] (22)

Once the numerical values of the even moments \( \{\mu_{2n}\} \) are known, \( \{a_{2n}\} \) can be calculated by making use of the relation (9) and then the normalized frequency distribution function is obtained from (7). In Fig. 4 the functions \( g(x) \) constructed with five even moments for the case of \( \lambda = 1 \) are shown for several \( a/R \). The
The value of $a/R$ is expressed in terms of percentage for the surface to volume ratio. From this figure it is observed that, as the surface to volume ratio is increased, the state density of low frequencies increases whereas that of high frequencies diminishes, exhibiting a tendency for the phonon softening. This softening is to be enhanced when the influence of anharmonicity is taken into account. Concerning the anharmonic surface vibration in metals, Hama and Matsubara have performed a detailed calculation of the surface relaxation and surface softening for an FCC metal Ni on the basis of the self-consistent Einstein model\textsuperscript{10}. According to them, the effective force constant for a surface atom may become nearly half of the bulk value for particular directions and at high temperature limit. Noting this result, we tentatively assume

$$\lambda = 1/2$$ \hspace{1cm} (23)

and calculate $g(x)$ including the anharmoni-
Note on Frequency Spectrum of Crystalline Fine Particles

The result is shown in Fig. 5 where remarkable enhancement of the phonon softening is manifested. Although the value of $\lambda$ assumed in (23) may be too small, we can recognize in Fig. 5 the importance of anharmonicity in the surface lattice vibration.

Fig. 5. Normalized frequency distribution function including anharmonic effect constructed with 5 even moments for various values of surface to volume ratio.

§ 5. Discussion

It is known that the moment-trace method is not always a good approach to the calculation of the spectrum and other properties of an infinite crystal. The convergence of the moment expansion for the frequency distribution function is slow due to the singularities which occur in the spectrum. The higher moments are heavily weighted with respect to one end of the spectrum, and very high accuracy is required in calculating the values of moments when we expect any extra information from the higher moments.

These defects inherent to the moment-trace method seem to be somewhat remedied in the case of crystalline fine particles: The sharp singularities in the spectrum disappear owing to the vanishing translational symmetry and the surface softening makes the frequency distribution shift to the low energy side, reducing the relative importance of the higher moments. In view of the fact that, except for computer simulation, it is not easy to work out theoretically the frequencies of the normal modes in crystalline fine particles, the method adopted in this paper would still provide us with an instructive and useful tool.

For reference, we present the normalized frequency distribution function calculated including the 6-th even moment which is extrapolated from the formula (21). Figure 6 is the result for the case of $\lambda=1$ and Fig. 7 for the case of $\lambda=1/2$. 
Since we can determine the moment $\mu_{12}$ only up to 3 significant figures, these curves might include large errors and not be trusted. However, it is interesting to observe that for the case of $\lambda=1/2$, where anharmonicity causes enhanced softening, there exists only small difference in $g(\nu)$ between the 5-moments calculation (Fig. 5) and the 6-moments result (Fig. 7).

We close the discussion by stating briefly how to incorporate the present results into a future generalization of theory of anharmonic lattice vibration in metallic fine particles. In this paper, we assume phenomenologically a surface force constant different from bulk value. More generally we start with a set of force constants and determine the frequency distribution function by the method same as this paper. Then the averaged Debye-Waller factor can be evaluated in terms of frequency spectrum. Now the thermally averaged effective potential should be determined including the Debye-Waller factor. Using this potential, we can discuss the surface relaxation and the changes in the force constants as have done by Hama and Matsubara for FCC metals. Thus we gain a new set of force
Note on Frequency Spectrum of Crystalline Fine Particles

constants and can re-start with the same calculation. In this way we have in principle a self-consistent scheme.

References