

ANHARMONIC CORRELATED DEBYE MODEL DEBYE-WALLER FACTOR COMPARED TO EINSTEIN MODEL RESULT

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ABSTRACT. An anharmonic correlated Debye model has been derived for vibrational amplitudes in the X-ray Absorption Fine Structure (XAFS). The model includes anharmonic effects based on Morse potential parameters. Analytical expression for Debye-Waller factor or second cumulant for different atomic shells has been derived. Numerical results for Cu approach those obtained by the anharmonic Einstein model. Both they contain zero-point contribution at low temperatures and linearly depend on the temperature at high temperatures as the classical limit values. They reflect the experimental results.

1. Introduction

The Debye-Waller (DW) factor $e^{-W(p)}$ accounts for the effects of the thermal vibration of atom in the theory of XAFS. The dominant term $W(p) = 2p^2\sigma^2$ depends on the mean square relative displacement (MSRD) [1-4], where p is photoelectron wave number. Anharmonic contribution included in the potential yields additional terms in the DW factors which if ignored can lead to non-negligible errors in structural parameters [4-11] extracted from XAFS spectra. The formalism for including anharmonic effects in XAFS is often based on cumulant expansion approach [4, 5]. Many efforts have been made [4-17] to include these anharmonic contributions, among them the anharmonic correlated Einstein model [16] avoids complicated calculations yet provides reasonable agreement with experiment.

This work is the next step of [15] to derive an anharmonic correlated Debye model for vibrational amplitudes in XAFS using quantum statistical theory. The model includes anharmonic effects based on the Morse potential parameters. Analytical expressions for DW factor or second cumulant for different atomic shells have been derived. Numerical results for Cu are compared to those obtained by the anharmonic Einstein model. Both they contain zero-point energy contribution at low temperatures and linearly depend on the temperature at high temperatures as the classical limit values, thus reflecting their experimental result behaviors [3, 6, 10].

2. Formalism

2.1. Anharmonic Einstein model for monatomic chain:

In this case we use the Morse potential expanded to the 3rd order about its equilibrium

$$V(x) = D(e^{-2ax} - 2e^{-ax}) \approx D(-1 + \alpha^2 x^2 - \alpha^3 x^3 + \dots), \quad (1)$$

where x is scaled relative deviation defined by $x = (l - a)/a$, l is instantaneous bond length between n th and $n+1$ th atoms and a is the equilibrium bond length between these two atoms. The Morse potential parameter α describes the width of the potential and D measures the dissociation energy.

Taking into account up to the 3rd order we obtain the potential

$$V(x) = -D + D\alpha^2 x^2 - D\alpha^3 x^3. \quad (2)$$

Using the definition $y = x - a$ or $x = y + a$ with $a = \langle x \rangle$ Eq. (2) is resulted as

$$\begin{aligned} V(x) &= -D + D\alpha^2 (y^2 + 2ay + a^2) - D\alpha^3 (y^3 + 3ay^2 + 3a^2y + a^3) \\ &= (D\alpha^2 - 3aD\alpha^3) y^2 - D\alpha^3 y^3 + 2aD\alpha^2 \left(1 - \frac{3}{2}a\alpha\right) y + (-D + D\alpha^2 a^2 - D\alpha^3 a^3). \end{aligned} \quad (3)$$

In the anharmonic Einstein model the interaction potential is given by

$$V(y) = \frac{1}{2} k_S y^2 - k_3 y^3 + V(a). \quad (4)$$

Comparing Eq. (3) to Eq. (4) we obtain the spring constant k_S , cubic parameter k_3

$$k_S = 2(D\alpha^2 - 3aD\alpha^3) \approx 2D\alpha^2 = M\omega_E^2; \quad k_3 = D\alpha^3, \quad (5)$$

Einstein frequency ω_E and temperature θ_E

$$\omega_E = \sqrt{\frac{k_S}{M}} = \sqrt{\frac{2D\alpha^2}{M}}; \quad \theta_E = \frac{\hbar\omega_E}{k_B} = \frac{\hbar}{k_B} \sqrt{\frac{2D\alpha^2}{M}}, \quad (6)$$

where M is mass of vibrating atom.

Atomic vibration is quantized as phonon and anharmonicity is the result of phonon-phonon interaction that is why we describe y by annihilation \hat{a} and creation \hat{a}^+ operators

$$y = \sigma_0 (\hat{a}^+ + \hat{a}), \quad \sigma_0 = \sqrt{\frac{\hbar}{2M\omega}} = \sqrt{\frac{\hbar\omega}{4D\alpha^2}}. \quad (7)$$

Using the calculation procedure as in [16] we obtain DW factor or second cumulant

$$\sigma^2 = \sigma_0^2 \frac{1+z}{1-z}; \quad \sigma_0^2 = \frac{\hbar\omega_E}{2k} = \frac{\hbar\omega_E}{4D\alpha^2}, \quad (8)$$

where $z = e^{-\theta_E/T}$ is temperature variable.

2.2. Anharmonic correlated Debye model for monatomic chain:

In this case the Morse potential Eq. (2) has the form

$$V(x) = D\alpha^2 x^2 - D\alpha^3 x^3 = V_0 + V_c, \quad (9)$$

where the harmonic contribution

$$V_0 = D\alpha^2 x^2 = D\alpha^2 \sum_n (u_{n+1} - u_n)^2, \quad (10)$$

and the anharmonic one

$$V_c = -D\alpha^3 \sum_n (u_{n+1} - u_n)^3, \quad (11)$$

are described in terms of the displacement u_n of n th atom. These displacements are related to phonon displacement operators A_k as shown by [18, 19]

$$u_n = \sqrt{\frac{\hbar}{2NM}} \sum_k \frac{e^{ikdn}}{\sqrt{\omega(k)}} A_k, \quad (12)$$

where A_k satisfies the following relation

$$A_k = A_{-k}^\dagger; \quad [A_k, A_{k'}] = 0, \quad (13)$$

and M is mass of composite atoms, $\omega(k)$ is the phonon spectrum of crystal momenta k , and N is the number of unit cells in the chain.

Based on the calculation procedure presented in [20, 21] we obtained the dispersion relation $\omega(k)$ as

$$\omega(k) = 2\sqrt{\frac{2D\alpha^2}{M}} \left| \sin\left(\frac{kd}{2}\right) \right|; \quad |kd| \leq \pi \quad (14)$$

The substitution of Eq. (12) into Eq. (10) yields

$$\begin{aligned} V_0 &= D\alpha^2 \sum_n \frac{\hbar}{2NM} \sum_k \left[\left(\frac{e^{ikd(n+1)} - e^{ikdn}}{\sqrt{\omega(k)}} A_k \right) \left(\frac{e^{ikd(n+1)} - e^{ikdn}}{\sqrt{\omega(k)}} A_k \right)^\dagger \right] \\ &= \frac{D\alpha^2 \hbar}{2NM} \sum_{n,k} \left[\frac{1}{\omega(k)} (e^{ikd(n+1)} - e^{ikdn}) (e^{-ikd(n+1)} - e^{-ikdn}) A_k A_k^\dagger \right] \\ &= \frac{D\alpha^2 \hbar}{2NM} N \sum_k \frac{2 - e^{ikd} - e^{-ikd}}{\omega(k)} A_k A_{-k} = \frac{D\alpha^2 \hbar}{M} \sum_k \frac{1 - \cos kd}{\omega(k)} A_k A_{-k}. \end{aligned} \quad (15)$$

Now we calculate DW factor for the nearest neighbor correlation denoted by index 1

$$\sigma^2 = \langle \Delta_1^2 \rangle_0 = \langle (u_{n+1} - u_n)^2 \rangle_0 \quad (16)$$

Applying the above results to Eq. (16) we obtain

$$\begin{aligned} \sigma^2 &= \left\langle \frac{\hbar}{2NM} \sum_{k,k'} \frac{e^{i(k+k')dn}}{\sqrt{\omega(k)\omega(k')}} (e^{ikd} - 1)(e^{ik'd} - 1) A_k A_{k'} \right\rangle_0 \\ &= \frac{\hbar}{2NM} \sum_{k,k'} \frac{e^{i(k+k')dn}}{\sqrt{\omega(k)\omega(k')}} (e^{ikd} - 1)(e^{ik'd} - 1) \langle A_k A_{k'} \rangle_0, \end{aligned} \quad (17)$$

where [19]

$$\langle A_k A_k \rangle_0 = \langle A_k(0) A_k(0) \rangle = -G_{k,k}^0(0), \quad A_k(t) = e^{iH_0} A_k e^{-iH_0}, \quad (18)$$

$$G_{k,k}^0(\tau) = \langle A_k(\tau) A_k(0) \rangle_0 = -\delta_{k,-k} \left\{ \langle n_k + 1 \rangle e^{-\hbar|\tau|\omega(k)} + \langle n_k \rangle e^{\hbar|\tau|\omega(k)} \right\}, \quad (19)$$

$$\langle n_k \rangle = \frac{1}{e^{\hbar\omega(k)/k_B T} - 1}, \quad (20)$$

and k_B is Boltzmann constant.

Substituting Eqs. (19), (20) into Eq. (18) we obtain

$$\begin{aligned} \langle A_k A_k \rangle_0 &= \delta_{k,-k} \left\{ \langle n_k + 1 \rangle + \langle n_k \rangle \right\} \\ &= \delta_{k,-k} \left(\frac{1}{e^{\frac{\hbar\omega(k)}{k_B T}} - 1} + 1 + \frac{1}{e^{\frac{\hbar\omega(k)}{k_B T}} - 1} \right) = -\delta_{k,-k} \frac{1 + e^{\frac{\hbar\omega(k)}{k_B T}}}{1 - e^{\frac{\hbar\omega(k)}{k_B T}}}, \end{aligned} \quad (21)$$

so that the DW factor is given by

$$\begin{aligned} \sigma^2 &= -\frac{\hbar}{2NM} \sum_k \frac{(e^{ikd} - 1)(e^{-ikd} - 1)}{\sqrt{\omega(k)\omega(-k)}} \frac{1 + e^{\frac{\hbar\omega(k)}{k_B T}}}{1 - e^{\frac{\hbar\omega(k)}{k_B T}}} = \frac{\hbar}{NM} \sum_k \frac{1 - \cos kd}{\omega(k)} \frac{1 + e^{\frac{\hbar\omega(k)}{k_B T}}}{1 - e^{\frac{\hbar\omega(k)}{k_B T}}} \\ &= \frac{\hbar}{NM} \sum_k \frac{2 \sin^2\left(\frac{kd}{2}\right)}{2\sqrt{\frac{2D\alpha^2}{M}} \left| \sin\left(\frac{kd}{2}\right) \right|} \frac{1 + e^{\frac{\hbar\omega(k)}{k_B T}}}{1 - e^{\frac{\hbar\omega(k)}{k_B T}}} = \frac{\hbar}{N\sqrt{2MD\alpha^2}} \sum_k \left| \sin\left(\frac{kd}{2}\right) \right| \frac{1 + e^{\frac{\hbar\omega(k)}{k_B T}}}{1 - e^{\frac{\hbar\omega(k)}{k_B T}}} \end{aligned} \quad (22)$$

which is described in terms of $\omega(k)$ as

$$\sigma^2 = \frac{1}{N} \sum_k \frac{\hbar\omega(k)}{4D\alpha^2} \frac{1 + e^{\frac{\hbar\omega(k)}{k_B T}}}{1 - e^{\frac{\hbar\omega(k)}{k_B T}}}. \quad (23)$$

For the limit of large N the summation over k can be replaced by the corresponding intergral

$$\sigma^2 = \frac{\hbar d}{\pi\sqrt{2MD\alpha^2}} \int_0^{\frac{\pi}{d}} \sin\left(\frac{kd}{2}\right) \frac{1 + e^{\frac{\hbar\omega(k)}{k_B T}}}{1 - e^{\frac{\hbar\omega(k)}{k_B T}}} dk = \frac{d}{\pi} \int_0^{\frac{\pi}{d}} \frac{\hbar\omega(k)}{4D\alpha^2} \frac{1 + e^{\frac{\hbar\omega(k)}{k_B T}}}{1 - e^{\frac{\hbar\omega(k)}{k_B T}}} dk. \quad (24)$$

This expression for DW factor approaches Eq. (8) obtained by the anharmonic Einstein model if all atoms vibrate by the same frequency, i., e., $\omega(k) = \omega_E = \text{const}$.

It is usually to consider the high temperature (HT) and low temperature (LT) limit using our derived Debye temperature

$$\theta_D = \frac{\hbar\omega_{\max}}{k_B} = \frac{2\hbar\alpha}{k_B} \sqrt{\frac{2D}{M}}. \quad (25)$$

In the HT limit ($T \gg \theta_D$) since $e^{-\frac{\hbar\omega(k)}{k_B T}} \approx 1 - \frac{\hbar\omega(k)}{k_B T}$ (26)

we obtain from

$$\sigma^2 = \frac{d}{\pi} \int_0^{\frac{\pi}{d}} \frac{\hbar\omega(k)}{4D\alpha^2} \frac{2 - \frac{\hbar\omega(k)}{k_B T}}{\frac{\hbar\omega(k)}{k_B T}} dk = \int_0^{\frac{\pi}{d}} \frac{dk_B T}{4\pi D\alpha^2} \left(2 - \frac{\hbar}{k_B T} 2\sqrt{\frac{2D\alpha^2}{M}} \sin\left(\frac{kd}{2}\right) \right) dk, \quad (27)$$

the HT limit equation

$$\begin{aligned} \sigma_{HT}^2 &= \frac{dk_B T}{2\pi D\alpha^2} k \Big|_0^{\pi/d} + \frac{2\hbar}{\pi\alpha\sqrt{2MD}} \cos\left(\frac{kd}{2}\right) \Big|_0^{\pi/d} = \frac{k_B}{2D\alpha^2} T - \frac{2\hbar}{\pi\alpha\sqrt{2MD}} \\ &= \frac{k_B}{2D\alpha^2} \left(T - \frac{\theta_D}{\pi} \right) \approx \frac{k_B}{2D\alpha^2} T \end{aligned} \quad (28)$$

which is linearly proportional to the temperature T .

In the LT limit ($T \approx 0$) it is approximated $e^{-\hbar\omega(k)/k_B T} \approx 0$ so that DW factor is given by

$$\sigma_{LT}^2 \approx \frac{d}{\pi} \int_0^{\frac{\pi}{d}} \frac{\hbar\omega(k)}{4D\alpha^2} dk = \int_0^{\frac{\pi}{d}} \frac{d\hbar}{4\pi D\alpha^2} 2\sqrt{\frac{2D\alpha^2}{M}} \sin\left(\frac{kd}{2}\right) dk = \frac{k_B \theta_D}{2\pi D\alpha^2} \neq 0. \quad (29)$$

which contains zero-point energy contribution.

The derived model can be generalized to calculate DW factors including correlation with other atomic shells $\rho = 2, 3, 4, 5, \dots$

$$\langle \Delta_\rho^2 \rangle_0 = \langle (u_{n+\rho} - u_n)^2 \rangle_0. \quad (30)$$

Applying expression for u_n to Eq. (17) we obtain

$$\begin{aligned} \sigma_\rho^2 &= \langle \Delta_\rho^2 \rangle_0 = \left\langle \frac{\hbar}{2NM} \sum_{k,k'} \frac{e^{i(k+k')an}}{\sqrt{\omega(k)\omega(k')}} (e^{i\rho kd} - 1)(e^{i\rho k'd} - 1) A_k A_{k'} \right\rangle_0 \\ &= \frac{\hbar}{2NM} \sum_{k,k'} \frac{e^{i(k+k')an}}{\sqrt{\omega(k)\omega(k')}} (e^{i\rho kd} - 1)(e^{i\rho k'd} - 1) \langle A_k A_{k'} \rangle_0 \\ &= \frac{\hbar}{NM} \sum_k \frac{1 - \cos \rho kd}{\omega(k)} \frac{1 + e^{-\frac{\hbar\omega(k)}{k_B T}}}{1 - e^{-\frac{\hbar\omega(k)}{k_B T}}} \end{aligned} \quad (31)$$

which is replaced by the corresponding intergral for the limit of large N

$$\sigma_\rho^2 = \langle \Delta_\rho^2 \rangle_0 = \frac{\hbar d}{\pi M} \int_0^{\frac{\pi}{d}} \frac{1 - \cos \rho kd}{\omega(k)} \frac{1 + e^{-\frac{\hbar\omega(k)}{k_B T}}}{1 - e^{-\frac{\hbar\omega(k)}{k_B T}}} dk. \quad (32)$$

3. Numerical results and discussion

Now we apply the expressions derived in previous section to numerical calculation for Cu. Morse potential parameters have been taken from [22, 23]. Figure 1 shows that the second cumulant or DW factor of Cu calculated by present anharmonic correlated Debye model and by anharmonic Einstein model contain zero-point energy contribution at low temperatures and linearly depends on the temperature at high temperature as the classical limit values. They reflect fundamental theoretical [4, 24] and experimental [3, 6, 10] result.

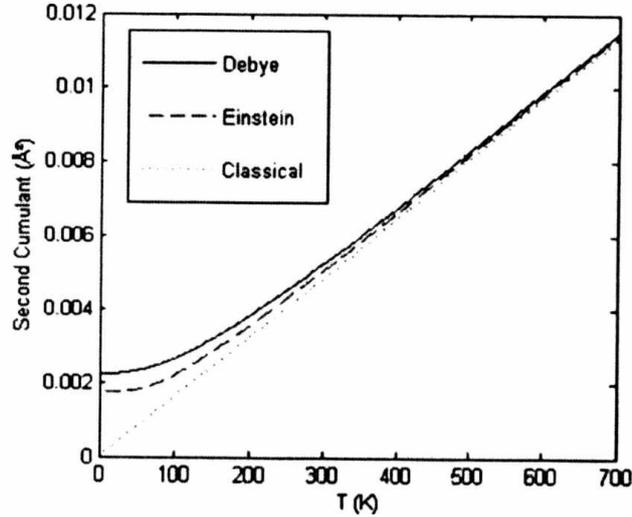


Figure 1: Comparison of DW factors for Cu calculated by anharmonic correlated Debye, Einstein models and by classical method.

Figure 2 illustrates the temperature dependence of DW factor of Cu calculated by present anharmonic correlated Debye model for different atomic shells. It is shown that the DW factor including correlation with the atoms located far from the absorbing atom increases as the shell number $n = \rho$ increases. But in this case the term containing $\cos(\rho kd)$ becomes a fastly oscillating function of k so that its contribution to correlation effect decreases. It is also clear that σ_ρ^2 will be divergent when $\rho \rightarrow \infty$ so that it is reduced to the one for vibration without correlation, that is why we often take the correlation only with neighboring atoms in a small cluster as in the anharmonic correlated Einstein model [16].

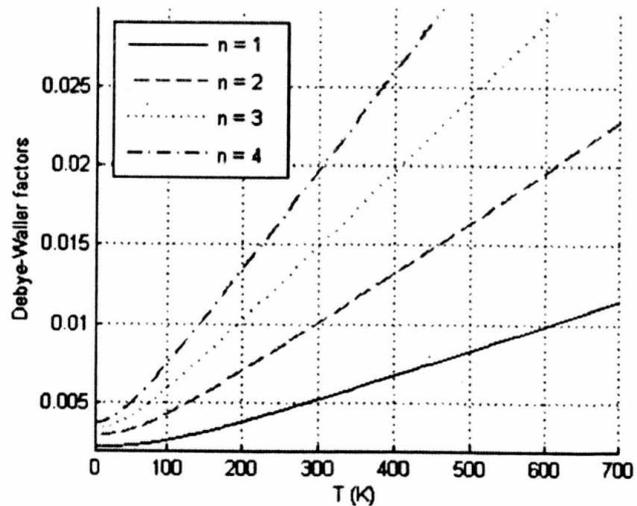


Figure 2: Temperature dependence of DW factors $\sigma_\rho^2(T)$ of Cu calculated by present anharmonic correlated Debye model for different atomic shells $n = \rho = 1, 2, 3, 4$.

4. Conclusions

In this work an anharmonic correlated Debye model has been developed including dispersion consideration. Analytical expression for the DW factor has been derived which reflects behaviors of fundamental theoretical and experimental results of this quantity.

Numerical results for Cu approach those obtained by the anharmonic Einstein model containing zero-point energy contribution at low temperature, and at high temperatures both they linearly depend on the temperature as the classical limit results.

Anharmonic correlated Debye model is more complicated than the Einstein one due to dispersion consideration, but it has the advantage for research when atoms in the substance vibrate by different frequencies.

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