
**PATH-INTEGRAL AND PERTURBATION METHODS FOR
DEBYE-WALLER FACTORS OBSERVED BY EXTENDED
X-RAY-ABSORPTION FINE STRUCTURE SPECTROSCOPY**

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Extended x-ray-absorption fine-structure spectroscopy provides information on the radial distribution function (RDF) around the x-ray absorbing atom in molecules and solids. The cumulants of RDF in gaseous Br₂ are evaluated using the second-order perturbation and path integral effective classical potential (ECP) methods, and the results are compared to the experimental data. As an application of the ECP method to solid surfaces, anisotropic and anharmonic vibration of thin Cu films is examined. The calculated results suggest that the out-of-planar vibration is more enhanced and more anharmonic than the lateral one, this being consistent with the experiments.

1 Introduction

Recently great attention has been paid to the temperature dependence of extended x-ray-absorption fine-structure (EXAFS), which provides information on thermal vibrations including anharmonicity. Experimentally, the EXAFS Debye-Waller factors or the cumulants of the radial distribution function (RDF) around the x-ray absorbing atom can be obtained. The theory concerning the relationship between the EXAFS cumulants and vibrational potentials has been developed based on the theories of quantum statistical first-order perturbation (P1) [1–5] and the path integral effective classical potential (ECP) [6–8]. The perturbation theory includes several intrinsic difficulties for practical use: complicated formulation and computation of many-atom systems and less reliability in large anharmonic systems. For instance,

the fourth-order cumulant from P1 is negative in the case of a positive fourth-order force constant and needs the second-order perturbation (P2) to yield meaningful results. On the other hand, the path integral ECP method [9] can appropriately overcome such difficulties in the P1 theory, although on the other hand the ECP method cannot describe quantum statistical anharmonicity at very low temperature.

Here, I will present the formulas of the EXAFS cumulants for diatomic systems using the P2 theory. This work was kindly motivated by Prof. Kleinert. When I visited Berlin in 1998, I showed him the ECP and P1 results. He was not satisfied with the results because he knew that the fourth-order cumulant requires the P2 theory and that the disagreement of the P1 result with the ECP theory and the experiment is trivial. He immediately suggested that I should derive the P2 formula. The P2 results given here are compared to those by the ECP theory and the experiment of the Br₂ molecule. I will also show my recent results concerning anisotropic and anharmonic vibration of surface atoms for thin Cu films calculated with the ECP method. The results are compared to our experimental data.

2 Diatomic Br₂

2.1 Second-Order Perturbation Formulas of the EXAFS Cumulants

Let us first derive the P2 formulas of the EXAFS cumulants for the diatomic system up to the fourth order. The thermal average of some physical quantity $\langle \mathcal{A} \rangle$ is expressed using a trace as

$$\langle \mathcal{A} \rangle = \frac{1}{Z} \text{Tr} \mathcal{A} e^{-\beta(\mathcal{H}_0 + \mathcal{H}')}, \quad (1)$$

where $Z = \text{Tr} e^{-\beta(\mathcal{H}_0 + \mathcal{H}')}$ is the partition function, \mathcal{H}_0 and \mathcal{H}' are the non-perturbed and perturbed Hamiltonian operators, respectively, and $\beta = (k_B T)^{-1}$ (k_B the Boltzmann constant and T the temperature). In the P2 perturbation, the trace is given as

$$\begin{aligned} \text{Tr} \mathcal{A} e^{-\beta(\mathcal{H}_0 + \mathcal{H}')} &\cong \text{Tr} \mathcal{A} e^{-\beta \mathcal{H}_0} \left(1 - \int_0^\beta \tilde{H}'(t_1) dt_1 \right. \\ &\quad \left. + \int_0^\beta \int_0^{t_1} \tilde{H}'(t_1) \tilde{H}'(t_2) dt_2 dt_1 \right), \end{aligned} \quad (2)$$

where $\tilde{H}'(\beta) = e^{\beta\mathcal{H}_0} \mathcal{H}' e^{-\beta\mathcal{H}_0}$. The partition function is obtained in a similar equation [$\mathcal{A}=1$ in Eq. (2)]. When the non-perturbed Hamiltonian is exactly solved, the second-order thermal average can be analytically evaluated.

The interatomic potential $V(r)$ in diatomic Br_2 is appropriately described by the fourth-order polynomial as

$$V(r) = \frac{1}{2}\kappa_0(r-r_0)^2 - \kappa_3(r-r_0)^3 + \kappa_4(r-r_0)^4 + \dots \quad (3)$$

Here, κ_0 , κ_3 , and κ_4 are the harmonic, third-order and fourth-order force constants, respectively. The second-order perturbation is important for even-order cumulants since the P1 and P2 terms provide the same order of magnitude. On the other hand, odd-order cumulants may be described within P1. The third- and fourth-order terms in Eq. (3) are regarded as a perturbed Hamiltonian, while the harmonic term can be used as a non-perturbed one. Using the eigenvalues and eigenfunctions of the non-perturbed harmonic oscillator, the integral of Eq. (2) is analytically evaluated. The second-order partition function is consequently obtained as

$$Z = Z^{(0)} + Z^{(1)} + Z^{(2)} + \dots, \quad (4)$$

$$\begin{aligned} Z^{(0)} &= \frac{1}{1-z}, \\ Z^{(1)} &= \frac{\kappa_4\sigma_0^4}{k_B T} \frac{3(1+z)^2}{(1-z)^3}, \\ Z^{(2)} &= \frac{\kappa_3^2\sigma_0^6}{(\hbar\omega)(k_B T)} \frac{11z^2 + 38z + 11}{(1-z)^3}, \end{aligned}$$

where $\omega = \sqrt{\kappa_0/\mu}$ (μ is the reduced mass), $\sigma_0^2 = \hbar/(2\mu\omega)$ (\hbar is the Planck constant divided by 2π), and $z = e^{-\beta\hbar\omega}$. The consequent formulas up to the fourth-order cumulant (P1 for C_1 and C_3 , and P2 for C_2 and C_4) are given as follows:

$$C_1 = \langle r - r_0 \rangle \cong C_1^{(1)} = \frac{6\kappa_3\sigma_0^4}{\hbar\omega} \frac{1+z}{1-z}, \quad (5)$$

$$C_2 = \langle (r - r_0 - C_1)^2 \rangle \cong C_2^{(0)} + C_2^{(1)} + C_2^{(2)}, \quad (6)$$

$$\begin{aligned} C_2^{(0)} &= \sigma_0^2 \frac{1+z}{1-z}, \\ C_2^{(1)} &= -\frac{\kappa_4\sigma_0^6}{\hbar\omega} \frac{12(1+z)^2}{(1-z)^2} - \frac{\kappa_4\sigma_0^6}{k_B T} \frac{24z(1+z)}{(1-z)^3}, \end{aligned}$$

$$C_2^{(2)} = \frac{\kappa_3^2 \sigma_0^8}{(\hbar\omega)^2} \frac{4(13z^2 + 58z + 13)}{(1-z)^2} + \frac{\kappa_3^2 \sigma_0^8}{(\hbar\omega)(k_B T)} \frac{24z(1+z)}{(1-z)^3},$$

$$C_3 = \langle (r - r_0 - C_1)^3 \rangle \cong C_3^{(1)} = \frac{\kappa_3 \sigma_0^6}{\hbar\omega} \frac{4(z^2 + 10z + 1)}{(1-z)^2}, \quad (7)$$

$$C_4 = \langle (r - r_0 - C_1)^4 \rangle - 3C_2^2 \cong C_4^{(1)} + C_4^{(2)}, \quad (8)$$

$$C_4^{(1)} = -\frac{\kappa_4 \sigma_0^8}{\hbar\omega} \frac{12(z^3 + 9z^2 + 9z + 1)}{(1-z)^3} - \frac{\kappa_4 \sigma_0^8}{k_B T} \frac{144z^2}{(1-z)^4},$$

$$C_4^{(2)} = \frac{\kappa_3^2 \sigma_0^{10}}{(\hbar\omega)^2} \frac{12(5z^3 + 109z^2 + 109z + 5)}{(1-z)^3} + \frac{\kappa_3^2 \sigma_0^{10}}{(\hbar\omega)(k_B T)} \frac{720z^2}{(1-z)^4}.$$

Note that the first-order perturbation terms of the even-order cumulants, $C_2^{(1)}$ and $C_4^{(1)}$ are negative, while $C_2^{(2)}$ and $C_4^{(2)}$ are positive.

2.2 Results

The EXAFS cumulants C_2 , C_3 , and C_4 for the intramolecular Br–Br shell were calculated numerically. The ECP formulation is omitted since it is fully established and found in the famous textbook of Prof. Kleinert [9]. The vibrational data [10] of $\kappa_0=2.459$ (mdyn/Å), $\kappa_3=1.756$ (mdyn/Å²) and $\kappa_4=1.058$ (mdyn/Å³) for Br₂ were employed. Figure 1 shows the ECP results, together with the P1 and P2 ones (the harmonic results are also given as HA for C_2). The classical and experimental EXAFS data are also plotted.

In the C_2 plot, the P1 result is slightly underestimated, especially at high temperature compared to the ECP one, because of a negative P1 value, while P2 agrees very well with ECP. Although C_4 is negative in P1, the P2 result approaches ECP. However, there seems to be still some underestimation for C_4 in P2 compared to ECP and this indicates that a higher-order perturbation calculation would be required.

In the case of C_3 , similar trends are observed. The P1 method estimates a little smaller value than ECP, again indicating a requirement of higher-order perturbation theory. The classical method shows essentially the same results as the ECP one at $T > 200$ K. As the temperature goes down from ~ 200 K, the classical value converges to zero monotonically as a function of T^2 and it gradually deviates from the two quantum statistical methods. This is caused by the zero-point anharmonicity. At $T < 100$ K, ECP begins to deviate from

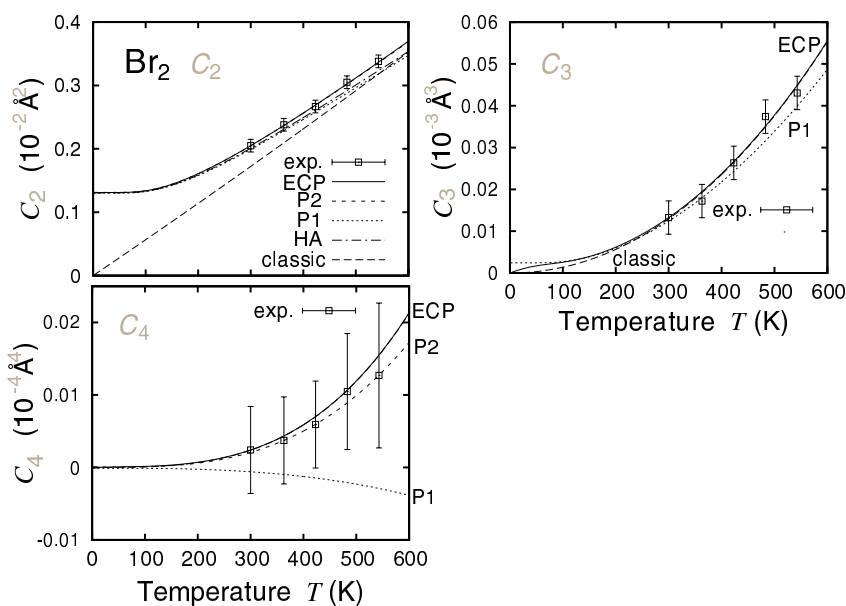


Figure 1. Temperature dependence of C_2 , C_3 , and C_4 of Br_2 evaluated by the ECP (solid lines), the classical (classic; long-dashed lines), and the P1 (dotted lines for C_2 , C_3 and C_4) and P2 (short-dashed lines for C_2 and C_4) methods, together with the experimental data (squares with error bars). For C_2 , the results of the harmonic approximation are also given (HA; dot-dashed line).

P1 and converges to zero at $T = 0$ K. In the present pair potential, there should be some finite (positive) C_3 at $T = 0$ K, implying that the P1 method predicts more appropriate C_3 at very low temperatures.

3 Anisotropic Vibration of a Thin Cu(111) Film

3.1 Computational Details

In the ECP calculations of bulk Cu, the formalism [12] is available within the low coupling approximation. The embedded-atom method (EAM) potential used here was taken from Ref. [11]. The normal vibrational analysis was initially performed to obtain the pure quantum mechanical fluctuations [12] using a cubic Brillouine zone $[-2\pi/a_0, 2\pi/a_0]$ (with the *fcc* lattice constant a_0) by sampling about 10^6 phonons. The classical-like *NPT* (constant pressure and temperature in a closed system) Monte Carlo (MC) calculations

were subsequently performed using the effective classical potential instead of the bare potential for 256 Cu atoms (4^3 *fcc* unit cells). Three-dimensional periodicity was imposed. 20 000 MC steps were calculated to reach the equilibrium and further 10 000 MC steps were performed to obtain the EXAFS cumulants, where each MC step contained 256-time movements of atoms and one-time variation of the lattice constant.

In the calculations of a thin Cu film, there exists no three-dimensional periodicity which leads to difficulties in applying the usual formula [12]. However, in order to obtain an estimation for the EXAFS cumulants to be compared with the experimental data, the quantum mechanical correction in ECP can be replaced by the bulk values, although this is rather crude from a pure theoretical point of view. This would give some overestimation of the vibrational amplitude of surface phonons at low temperature since the eigenfrequencies should be smaller than the bulk ones. Within this approximation, the ECP calculations can be similarly performed. A six-layer Cu(111) film was assumed, where each layer contained 48 atoms in a rectangular lattice and the lowest layer was assumed to be vibrationally fixed. Similar *NPT* MC simulations were performed to obtain the EXAFS cumulants of intra- and interlayer atom pairs.

3.2 Results

The calculated EXAFS cumulants for the first-nearest neighbor (NN) Cu-Cu shell of bulk Cu and the thin Cu(111) film are shown in Fig. 2. Therein, the obtained quantities for each layer are separately given for the thin film. Note that the first-and-second layer (12) distance as well as all the intra-layer distances, i.e. 11, 22, 33, and 44, are contracted compared to the bulk one, while the second-and-third (23) and third-and-fourth (34) layer distances are elongated. The thermal expansion, C_2 and C_3 are found to be significantly enhanced for the first-and-second layer.

When comparing the present theoretical results with the experimental data [14], polarization dependent Cu (and also Ni) *K*-edge EXAFS spectra were taken for ultrathin Cu(111) [or Ni(111)] films grown epitaxially on HOPG (highly oriented pyrolytic graphite) by varying the thickness. By using the results of thickness dependence of anisotropic C_2 and C_3 , the surface out-of-planar and in-planar components can be extracted. Moreover, by assuming (roughly) that all other contributions than the in-planar first-and-first (11) and the out-of-planar first-and-second (12) ones are equal to the bulk

Table 1. Effective Debye temperature Θ_D and difference of the third-order EXAFS cumulants ΔC_3 (difference between 100 and 300 K) for the surface out-of-planar, surface in-planar and bulk vibrations. Both experimental and theoretical results are given.

| | out-of-plane | | in-plane | | bulk | |
|--------|--------------|--------------|------------|--------------|------------|--------------|
| | Θ_D | ΔC_3 | Θ_D | ΔC_3 | Θ_D | ΔC_3 |
| Calc. | 272 | 3.65 | 290 | 2.47 | 313 | 1.48 |
| Exptl. | 262(25) | 3.8(8) | 322(30) | 3.1(6) | 338 | 1.62 |

one, three components of 11, 12 and bulk were successfully determined. For detailed procedures of the data analysis see Ref. [14]. The results are summarized in Table 1. In the experimental work, the obtained quantities are the difference between 100 and 300 K. For C_2 , the ΔC_2 values are replaced by the effective Debye temperature Θ_D , which is similarly evaluated by using the correlated Debye model [13]. Although the difference between the out-of-planar and in-planar vibrations is underestimated in the calculations, both results agree well with each other semi-quantitatively. It is concluded both experimentally and theoretically that the surface out-of-planar vibration is significantly softer and more anharmonic than the inner, lateral or bulk ones. As a reason for the underestimation in the calculations, one can suppose that the present theoretical calculations treat perfect films, while the actual films should contain many defects and some roughening might occur already at room temperature. This is indicated by the experimental findings [14] of smaller coordination number and larger C_2 . Since the surface area becomes wider in the presence of defects, the surface Debye temperature would effectively be lowered. One should also note that the surface Debye temperature of Cu(100) determined by LEED (low energy electron diffraction) [15] is 235 K, which is still lower than the EXAFS result of 262 K.

It is essentially important to recall intrinsic differences between EXAFS and diffraction. The diffraction techniques such as LEED provide information on absolute displacements with respect to the lattice, while EXAFS gives relative ones between x-ray absorbing and neighboring atoms. Although within the correlated Debye model the Debye temperature should be equal to the one given by the diffraction, C_2 and C_3 are the parameters obtained uniquely by EXAFS. It is natural that the out-of-planar vibration is enhanced at the

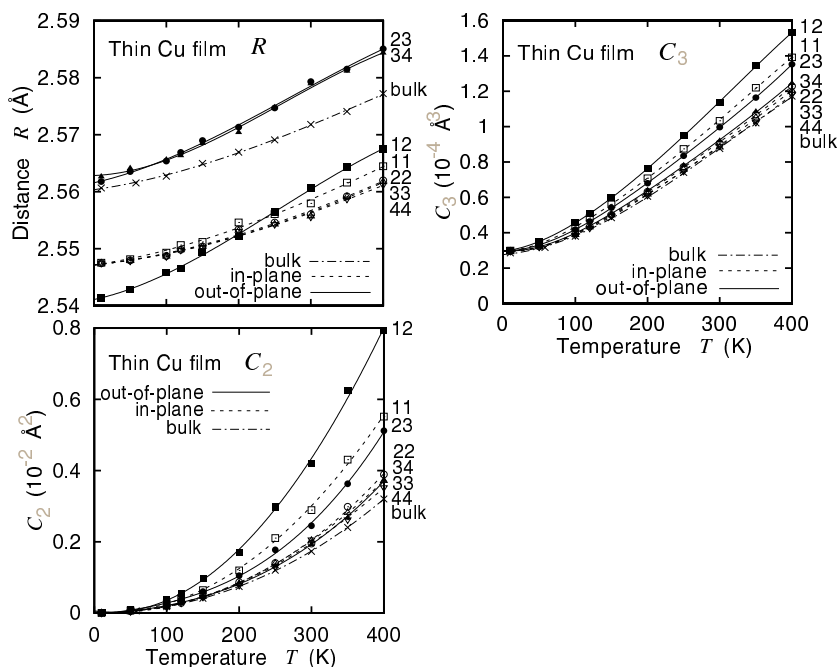


Figure 2. Temperature dependence of the interatomic distance R and the second- and third-order cumulants, C_2 and C_3 , for several first-NN Cu-Cu shells in a 6 ML Cu(111) film, together with the bulk values. For instance, 11 implies the first-and-first intra-layer distance, while 12 indicates the first-and-second interlayer distance (11: open square; 22: open circle; 33: upward triangle; 44: downward triangle; 12: filled square; 23: filled circle; 34: filled upward triangle; intra-layer: dashed line; interlayer: solid line; bulk: cross and dot-dashed line).

surface as long as the absolute displacement is discussed. This is simply ascribed to a lack of atoms upwards at the surface. On the contrary, from a local point of view, the out-of-planar motion is not always enhanced as can be seen in Refs. [16,17]. In the $p4g(2 \times 2)\text{N}/\text{Ni}(001)$ surface, the out-of-planar N-Ni bond was found to be much stiffer and less anharmonic than the lateral ones [16], and similarly the out-of-planar S-Ni bond in $c(2 \times 2)\text{S}/\text{Ni}(110)$ is stiffer and less anharmonic than the lateral ones [17]. In the present case, the surface out-of-planar bond is found to be weaker and more anharmonic than the in-planar one. The aim of this work is to obtain a hint of surface melting, which is an initial stage of bulk melting. The enhancement of the vibrational amplitude and anharmonicity along the surface normal is an important con-

clusion since a roughening transition should occur through the hopping of surface atoms for which not only the amplitude but also the anharmonicity is essential.

4 Discussion and Conclusions

In the present calculations for a one-dimensional system of Br_2 , some disadvantage of the ECP method was seen in the estimation of C_3 at low temperature. In Fig. 1(b), a strange decrease in $C_3(\text{ECP})$ was found at a temperature less than ~ 100 K. This is because in the ECP method the vibrational properties tend to be harmonic at the 0 K limit. It should also be true for C_4 , although C_4 is essentially zero and less important at low temperature. The perturbation theory can predict C_3 more accurate at low temperature. The ECP method is not reliable for strong quantum systems. In order to obtain such information, one has to perform quantum statistical perturbation calculations or more sophisticated path-integral Monte Carlo simulations. At higher temperatures, however, the P1 and P2 theory is insufficient to describe appropriate anharmonicity. Higher-order expansion would be required, and in the EXAFS analysis of usual systems common low-temperature anharmonicity is not very important. It can be concluded that the ECP method is more practical and reliable for most systems with one degree of vibrational freedom as well as many degrees of freedoms.

In summary, the ECP theory can treat the quantum effect, anharmonicity, many degrees of vibrational freedom, three-dimensional periodicity, higher-NN interaction and many-body interaction. It is essentially difficult or impossible to include all the contributions to other theories, at least in a practical sense of numerical calculations. It is also noted again that the EAM matches the ECP theory excellently, this allowing to investigate vibrational properties of metals quantum statistically.

In the simulations of thin Cu(111) film, thermal vibration and local thermal expansion are larger than those for their corresponding bulk metals. The relative motions focused on the surface local bonds are enhanced in the surface normal direction. These findings are consistent with the EXAFS experiments. The enhanced vibrational amplitude and anharmonicity in the surface normal direction could be a trigger of a roughening transition, surface melting, and consequent bulk melting.

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References

- [1] H. Rabus, Ph.D. thesis (Department of Physics, Freie Universität Berlin, 1991).
- [2] A.I. Frenkel and J.J. Rehr, *Phys. Rev. B* **48**, 585 (1993).
- [3] T. Fujikawa and T. Miyanaga, *J. Phys. Soc. Jpn.* **62**, 4108 (1993).
- [4] T. Yokoyama, K. Kobayashi, T. Ohta, and A. Ugawa, *Phys. Rev. B* **53**, 6111 (1996).
- [5] T. Yokoyama, Y. Yonamoto, T. Ohta, and A. Ugawa, *Phys. Rev. B* **54**, 6921 (1996).
- [6] T. Fujikawa, T. Miyanaga, and T. Suzuki, *J. Phys. Soc. Jpn.* **66**, 2897 (1997).
- [7] T. Yokoyama, *Phys. Rev. B* **57**, 3423 (1998).
- [8] T. Yokoyama, *J. Synchrotron Radiat.* **6**, 323 (1999).
- [9] H. Kleinert, *Path Integrals in Quantum Mechanics, Statistics, and Polymer Physics*, 2nd ed. (World Scientific, Singapore, 1995).
- [10] K.P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure IV: Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).
- [11] S.M. Foiles, M.I. Basks, and M.S. Daw, *Phys. Rev. B* **33**, 7983 (1986).
- [12] A. Cuccoli, R. Giachetti, V. Tognetti, R. Vaia, and P. Verrucchi, *J. Phys. Condens. Matter* **7**, 7891 (1995).
- [13] G. Beni and P.M. Platzman, *Phys. Rev. B* **14**, 1514 (1976).
- [14] M. Kiguchi, T. Yokoyama, D. Matsumura, O. Endo, H. Kondoh, and T. Ohta, *Phys. Rev. B* **61**, 14020 (2000).
- [15] S. Müller, A. Kinne, M. Kottcke, R. Metzler, P. Bayer, L. Hammer, and K. Heinz, *Phys. Rev. Lett.* **75**, 2859 (1995).
- [16] L. Wenzel, D. Arvanitis, H. Rabus, T. Lederer, K. Baberschke, and G. Comelli, *Phys. Rev. Lett.* **64**, 1765 (1990).
- [17] T. Yokoyama, H. Hamamatsu, Y. Kitajima, Y. Takata, S. Yagi, and T. Ohta, *Surf. Sci.* **313**, 197 (1994).