

Real space approach to thermal factors in EXAFS for strong anharmonic systems

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Thermal effects in EXAFS due to atomic vibration are studied by use of the path integral approach. This approach can be applied to strong anharmonic systems, where the cumulant analyses break. This paper describes some results applied to one-dimensional systems with double-well potential and Morse potential. For both systems, quantum tunneling effect plays an important role in EXAFS thermal factor.

Keywords: EXAFS, Debye-Waller factors, path integral, cumulant expansion, anharmonic vibration

1. Introduction

Theoretical aspects of temperature dependence in EXAFS have been studied within the framework of harmonic vibration and some improvements have been found beyond the harmonic approximation with perturbation theory (Tranquada & Ingalls, 1983, Fujikawa & Miyanaga, 1993, Yokoyama, *et al.*, 1996). The perturbation approaches are useful to describe weak anharmonicity in the analyses of temperature effects in EXAFS and they have provided interesting information based on cumulant expansion. On the other hand real space approaches (Yokoyama, *et al.*, 1989 and Dalba, *et al.*, 1995) have been widely used classically to relate the EXAFS Debye-Waller factors to interatomic potential. In this paper we apply the path integral approach to the EXAFS thermal factors of diatomic systems vibrating quantum mechanically in strongly anharmonic systems with a double-well potential and Morse potential.

2. Basic Theory

Let consider diatomic systems in a reservoir at temperature T whose relative vibrational motion is described by the Hamiltonian,

$$H = \frac{p^2}{2\mu} + V(q), \quad (2.1)$$

where μ is the reduced mass and q is the instantaneous interatomic distance. When we deal with statistical average of an operator A , we should calculate the trace $\langle A \rangle = \text{Tr}(A\rho)/Z$, where ρ is the density operator defined by $\rho = \exp(-\beta H)$, $\beta = 1/k_B T$, and $Z = \text{Tr}(\rho) = \text{Tr}(\exp(-\beta H))$ is the partition function for the system. The trace can be calculated by applying Feynman's path integral techniques, however, instead of summing over all paths in just one step, one can classify the paths into two groups as proposed by Feynman (Feynman, 1972). One group consists of average (quasi classical) path given by

$$\bar{q} = \int_0^\beta \langle u \rangle du / \beta, \quad (h = 1) \quad (2.2)$$

and the other group consists of quantum fluctuation around \bar{q} . The average path is the same as the classical path in the high temperature limit ($\beta \rightarrow 0$). To use the non-perturbation method based on the path-integral technique, we approximate the instantaneous potential $V(q(u))$ by a trial potential quadratic in the fluctuation path $q - \bar{q}$ (Cuccoli, *et al.*, 1995)

$$V \sim V_0(q, \bar{q}) = w(\bar{q}) + \mu \omega(\bar{q})^2 (q - \bar{q})^2 / 2. \quad (2.3)$$

Now the parameters $w(\bar{q})$ and $\omega(\bar{q})$ are to be optimized so that the trial reduced density well approximates the true reduced density. Final expression for the average of a local operator A can be represented in terms of the probability density $P(q)$ just like a classical statistical mechanics (from now on q is used instead of \bar{q} for brevity),

$$\langle A \rangle = \int A(q) P(q) dq \quad (2.4)$$

This expression, however, includes the important quantum effects, and the probability density is represented by

$$P(q) = \frac{1}{Z} \sqrt{\frac{\mu}{2\pi\beta}} \exp[-\beta V_L(q)] \quad (2.5)$$

where the local effective potential $V_L(q)$ is obtained from the self-consistent requirement in terms of $w(\bar{q})$ and $\omega(\bar{q})$. In the EXAFS analyses the operator A should be $\exp(2ik\Delta q)$, where k is the wave vector of an ejected photoelectron, $k = |\mathbf{k}|$ and Δq is the projected relative displacement which is simply given by $\Delta q = q - q_0$ (q_0 is the equilibrium interatomic distance) in one-dimensional cases. So that what we should calculate to study EXAFS thermal factors is

$$g(k) = \langle \exp(2ikq) \rangle = \int_{-\infty}^{\infty} \exp(2ikq) P(q) dq \quad (2.6)$$

in the plane wave approximation. When all of the integrals in the cumulants and also the cumulant expansion converge, the thermal damping function $g(k)$ can be written,

$$g(k) = \exp\{-2k^2 \langle q^2 \rangle_c + \frac{2}{3}k^4 \langle q^4 \rangle_c - \dots\} \\ \times \exp\{i\{k \langle q \rangle_c - \frac{4}{3}k^3 \langle q^3 \rangle_c + \dots\}\} \quad (2.7)$$

3. Application to Diatomic System

We now consider a strongly anharmonic system with double-well potential

$$V(q) = \epsilon(q^2 - \sigma^2) \quad (3.1)$$

At $q = \pm\sigma$ the absolute minimum of V , $V(q)_{\min}=0$ is given. An important parameter to describe quantum effects is \bar{g} defined by $\omega_0 / \epsilon\sigma^2$; the case of weak (strong) quantum effects occur when \bar{g} is small (large). In the following applications we shall use the unit, $\sigma = m = 1$ for simplicity. Figure 1 shows $\langle q^2 \rangle_c$ as a function of temperature for $\bar{g} = 5$ with the classical result (dotted line). The classical particle in double well potential is frozen at the one of the bottom of the potential well, at $q = \pm 1$, so $\langle q^2 \rangle_c = 1$ at $T=0$. Of course the classical approximation does not work at such a low temperature, and tunneling effect play an important role through the potential barrier at $q=0$.

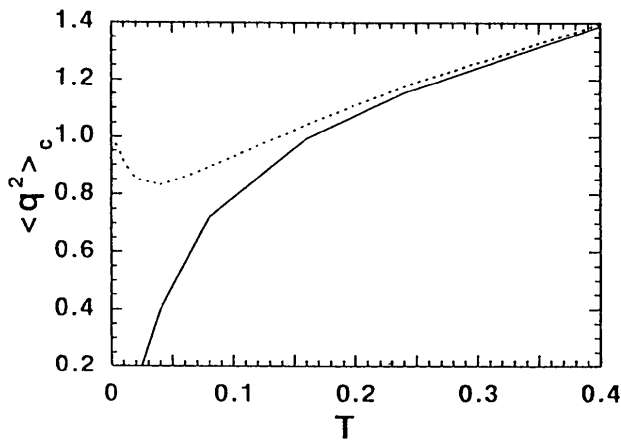


Figure 1
The temperature dependence of the quantum (solid line) and classical (dotted line) second order cumulant $\langle q^2 \rangle_c$ for the double-well potential at $\bar{g}=5$.

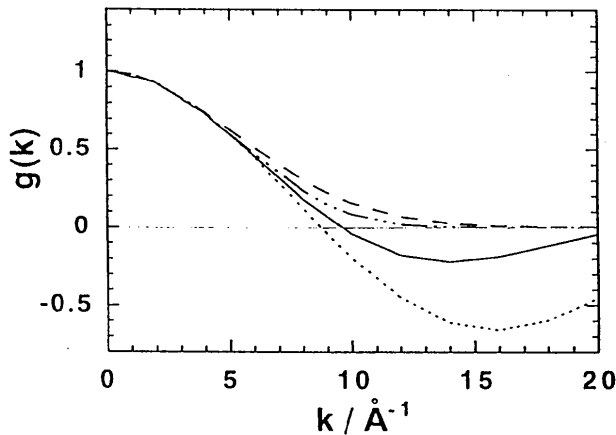


Figure 2
The quantum (solid line) and classical (dotted line) damping function $g(k)$ for Cu-O system with double-well potential at 80 K. The cumulant expansion for $g(k)$ are also shown up to second order (dashed line) and fourth order (three-dots-dashed line).

Figure 2 shows the damping function $g(k)$ as a function of k at the temperature $T=80$ K for Cu-O atomic pair in $\text{YBa}_2\text{CuO}_{7-d}$. Several experimental results indicate that the axial oxygen atom moves in a double-well potential (Mustrede Leon *et al.*, 1993). The calculated results show that neither the cumulant expansion nor the classical approximation work well at 80 K. It is noted that the phase inversion is observed at high k in $g(k)$.

Next we discuss the thermal effects in EXAFS for a Morse potential;

$$V(q) = D[e^{-2\Gamma(q-q_0)} - 2e^{-\Gamma(q-q_0)}] \quad (3.2)$$

where the parameter D describes the depth and Γ the curvature of the potential. The Morse potential is asymmetric around the equilibrium position q_0 and the thermal factor for the EXAFS should be complex. Figure 3 shows the probability densities compared with those in the classical approximation for this potential with $D=1$ (except for three dot-dashed line where $D=5$ is assumed: the small (large) D corresponds to large (small) quantum effect), $\Gamma=0.1 \text{\AA}^{-1}$, $q_0=2.5 \text{\AA}$ and the reduced temperature $t (=k_B T/D) = 0.02$. For a typical value of D is 0.8 eV; $T=186$ K is obtained for $t=0.02$. The quantum effects contribute to the broadening of the peak and the quantum probability distribution shifts its maximum position to 2.6\AA because of the tunneling effects.

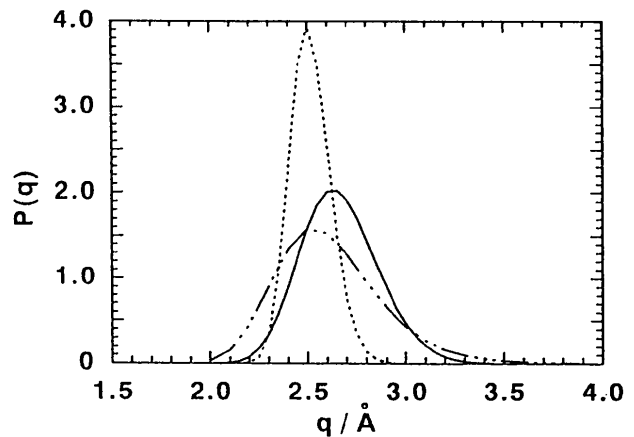


Figure 3
The quantum (solid line) and the classical (dashed line) probability density functions for the Morse potential at high temperature $t = 0.02$ for $D=1$. Three dot-dashed line represents that for $D=5$.

Figure 4(a) shows the damping function $|g(k)|$ corresponding to $P(q)$ in Fig. 3, where the results for the cumulant approximations are also shown for comparison. Both of the cumulant expansions up to the second order and up to the fourth order terms give satisfactory results in particular the latter result is good enough, whereas the classical approximation gives a poor result. Figure 4(b) shows the phase functions. The first order cumulant gives a linear function of k , which is poor approximation for large k . If we take the third order cumulant into account, the result is much improved. The classical approximation, on the other hand, is quite bad for the phase

factor, too. The results for $D=5$ are also shown in Fig. 4. In Fig. 4(a) the small D ($D=1$) gives the result close to the classical approximation, though the strong quantum effects are expected. The decay of $|g(k)|$ is rapid for large D as a function of k because the probability density $P(q)$ for large D is broader than that for small D as shown in Fig. 3. On the other hand $\varphi(q)$ for small D shows the large deviation from the classical phase function in the low energy region, because the peak shift in $P(q)$ is larger for $D=1$ than that for $D=5$.

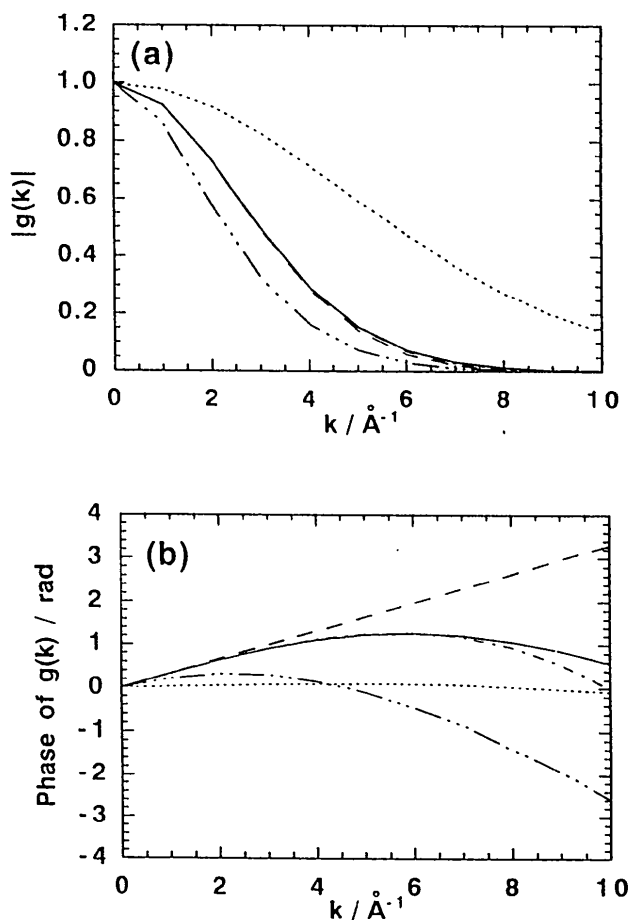


Figure 4

(a) EXAFS thermal damping function $|g(k)|$ and (b) phase $j(k)$ as a function of k for the quantum result (solid line) and the classical approximation (dashed line) at $t=0.02$. The results for the cumulant expansion are also shown for up to the second (first) order by the long dashed lines and up to the fourth (third) order by dash-dotted lines in (a) ((b)). Three dot-dashed lines in (a) and (b) represent the quantum results for $D=5$.

4. Conclusion

The real space approach based on finite temperature path integral theory is applied to the strongly anharmonic systems as double-well and Morse potentials, and the applicability of the classical and the cumulant approximation is studied. In both cases the tunneling effects play an important role at low temperature, there the classical approximation cannot be applied but the cumulant approximation gives the reasonable results. For the asymmetric potential, thermal effects appear in both the damping function and the phase function. The phase is rather sensitive to temperature than the thermal damping.

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