Thermal expansion and x-ray-absorption fine-structure cumulants

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In the classical limit, a simple relation has been shown to exist between the thermal expansion coefficient α and the cumulants of the vibrational amplitude that are measured in x-ray-absorption fine structure (XAFS), i.e., $\alpha r T \sigma^2 / \sigma^{(3)} = 1/2$, where σ^2 is the mean-square vibrational amplitude, $\sigma^{(3)}$ the third cumulant, T the absolute temperature, and r the equilibrium bond length. We generalize this relation to the quantum case using a correlated Einstein model and thermodynamic perturbation theory, and find $\alpha r T \sigma^2 / \sigma^{(3)} = [3z(1 + z) \ln(1/z)] / [(1 - z)(1 + 10z + z^2)]$, where $z = \exp(-\Theta_E / T)$, and Θ_E is the Einstein temperature. This result is found to be in agreement with the measured thermal expansion coefficient and XAFS cumulants in RbBr at 30 K and 125 K.

I. INTRODUCTION

Within the harmonic approximation the temperature dependence of the x-ray-absorption fine-structure (XAFS) amplitude is governed by a Gaussian Debye-Waller factor $\exp(-2p^2\sigma^2)$, where σ^2 is the mean-square vibrational amplitude and p is the photoelectron wave number. Anharmonic terms in the potential give rise to a correction in the XAFS phase $\delta\Phi = -(4/3)p^3\sigma^{(3)}$, where $\sigma^{(3)}$ is the third cumulant of the vibrational amplitude distribution.[1] This contribution leads to an unphysical, apparent contraction with increasing temperature unless it is properly accounted for.[2] Recently a simple relation between the thermal expansion coefficient $\alpha = (1/r)dr(T)/dT$ and the second and third cumulants was deduced for the high-temperature limit of a simple anharmonic oscillator model,[3]

$$\frac{\alpha r T \sigma^2}{\sigma^{(3)}} = \frac{1}{2}, \tag{1}$$

where T is the absolute temperature and r is the equilibrium bond length. An analogous classical relation $r(T) - r(0) = \sigma^{(3)}/2\sigma^2$ was obtained by Wenzel *et al.*[4] and is implicit in the work of Stern and Heald.[5] These relations were found to be in accord with experiment[3,4] in the classical limit.

In this work we generalize these relations to low temperatures and compare the results with experiment. To simplify the problem as much as possible we make use of an anharmonic, correlated-Einstein model, i.e., an oscillator with a single frequency taken to be the mean of the local density of modes that contribute to the relative vibrational amplitude of a given bond,[6] plus a small anharmonic perturbation. This Einstein frequency ω_E depends on the bond in question, and is typically some fraction of the corresponding Debye frequency $\omega_D = k_B \Theta_D / \hbar$.

We find that the relation between these cumulants and the thermal expansion coefficient is not generally a simple ratio but, rather, a temperature dependent function of T/Θ_E, where Θ_E is the Einstein temperature. Like all Einstein models, this model fails to give the correct power-law temperature dependence of various thermodynamic quantities near $T = 0$, but such differences are usually difficult to distinguish experimentally. However, because the long-wavelength acoustic modes do not contribute to the relative motion of a given bond, the Einstein model is a better approximation for bond vibrational amplitudes than for site amplitudes.

II. FORMALISM

We consider the vibration of two masses M_1 and M_2, interacting via an anharmonic potential $V(x)$,

$$V(x) = \frac{1}{2}k_0 x^2 + k_3 x^3 + \cdots, \tag{2}$$

where x is the deviation of the bond length r from the location of the potential minimum, i.e., $x = r - r_0$. We define y to be the deviation from the equilibrium value of x at temperature T and determine the net thermal expansion $a(T) = \langle r - r_0 \rangle$ by setting $\langle x - a \rangle = \langle y \rangle = 0$, where the brackets denote a thermal average. Our calculations of these averages are based on the quasi-harmonic approximation, in which the Hamiltonian of the system is written as a harmonic term with respect to the equilibrium position at a given temperature, plus an anharmonic perturbation:

$$H = \frac{p^2}{2\mu} + V(x) \equiv H_0 + V(a) + \delta V(y), \tag{3}$$

where $1/\mu = 1/M_1 + 1/M_2$, and

$$H_0 = \frac{p^2}{2\mu} + \frac{1}{2}ky^2,$$

$$\delta V(y) = (k_0 a + 3k_3 a^2)y + k_3 y^3. \tag{4}$$

Here the effective spring constant $k = k_0 + 6k_3 a = \mu\omega^2$. Note that the length dependence of k yields a Grüneisen parameter $\gamma = -\partial \ln\omega/\partial \ln V = -rk_3/k$.

We now use first-order thermodynamic perturbation theory[7] to derive expressions for the net thermal expansion a, and for the second and third cumulants, to leading order in k_3:

$$0 = \langle y \rangle = \frac{1}{Z} \operatorname{Tr} \rho\, y \cong \frac{1}{Z_0} \operatorname{Tr} \delta\rho\, y, \tag{5}$$

$$\sigma^2 = \langle y^2 \rangle = \frac{1}{Z} \operatorname{Tr} \rho\, y^2 \cong \frac{1}{Z_0} \operatorname{Tr} \rho_0\, y^2, \tag{6}$$

$$\sigma^{(3)} = \langle y^3 \rangle = \frac{1}{Z} \operatorname{Tr} \rho\, y^3 \cong \frac{1}{Z_0} \operatorname{Tr} \delta\rho\, y^3. \tag{7}$$

Here the brackets denote a thermal average over the statistical density matrix $\rho = e^{-\beta H}$ and $Z = \operatorname{Tr}\rho$ is the canonical partition function; the corresponding unperturbed quantities are $\rho_0 = e^{-\beta H_0}$ and $Z_0 = \operatorname{Tr}\rho_0$. This first-order treatment ignores anharmonic contributions to σ^2, which only arise in second order, but is adequate to account for the low-temperature behavior discussed below. To leading order in the perturbation δV, $\rho = \rho_0 + \delta\rho$ where $\delta\rho$ is given by[7]

$$\delta\rho = -\int_0^\beta e^{-\beta H_0} \delta\tilde{V}(\beta')\mathrm{d}\beta', \tag{8}$$

$\delta\tilde{V}(\beta) = e^{\beta H_0}\delta V e^{-\beta H_0}$, $\beta \equiv 1/k_B T$, and k_B is Boltzmann's constant.

The traces in Eqs. (5)–(7) are straightforwardly evaluated using harmonic oscillator states $|n\rangle$ with eigenvalues $E_n = n\hbar\omega$ (for convenience we set the zero point energy to zero). Thus,

$$Z_0 = \sum_n e^{-n\beta\hbar\omega} = \sum_{n=0}^\infty z^n = \frac{1}{1-z}, \tag{9}$$

where the temperature variable $z \equiv e^{-\beta\hbar\omega} = e^{-\Theta_E/T}$, and $\Theta_E = \hbar\omega/k_B$ is the Einstein temperature. Similarly

$$\langle y^2 \rangle = \frac{1}{Z_0} \sum_n e^{-n\beta\hbar\omega} \langle n|y^2|n\rangle. \tag{10}$$

To evaluate the matrix elements, we express y in terms of creation and annihilation operators, $\hat{a}$ and $\hat{a}^\dagger$, i.e., $y \equiv \sigma_0(\hat{a} + \hat{a}^\dagger)$, where $\sigma_0 = \sqrt{\hbar/2\mu\omega}$. These operators have the following properties: $[\hat{a},\hat{a}^\dagger] = 1$, $\hat{a}^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle$, and $\mathbf{n}|n\rangle = n|n\rangle$ where $\mathbf{n} = \hat{a}^\dagger\hat{a}$ is the number operator. Thus, for example, $\langle n|y^2|n\rangle = \sigma_0^2\langle n|\hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a}|n\rangle = (2n+1)\sigma_0^2$, so that

$$\sigma^2 = \frac{\sigma_0^2}{Z_0} \sum_n z^n(2n+1) = \frac{\hbar\omega}{2k}\frac{1+z}{1-z}, \tag{11}$$

where we have used $\sum_n nz^n = z/(1-z)^2$. On performing the integral in Eq. (8) over β' and evaluating the traces, the remaining odd moments are given by

$$\langle y^m \rangle = \frac{1}{Z_0} \sum_{nn'} \frac{e^{-\beta E_n} - e^{-\beta E_{n'}}}{E_n - E_{n'}} \langle n|\delta V(y)|n'\rangle\langle n'|y^m|n\rangle. \tag{12}$$

Since $\delta V(y) \cong k_0 a y + k_3 y^3$ to leading order in k_3 and $m = 1$ or 3, the matrix elements only couple n to $n \pm 1$, $n \pm 3$. Also, making use of the hermiticity of δV and y^m, one can easily demonstrate the equivalence of the $n' = n \pm j$ terms in Eq. (12). Thus we need only the matrix elements,

$$\langle n|y|n+1\rangle = \sigma_0(n+1)^{1/2},$$

$$\langle n|y^3|n+1\rangle = 3\sigma_0^3(n+1)^{3/2}, \tag{13}$$

$$\langle n|y^3|n+3\rangle = \sigma_0^3[(n+1)(n+2)(n+3)]^{1/2}.$$

Hence

$$\langle y \rangle = \frac{-2(1-z)}{Z_0\hbar\omega}\left(k_0\, a\sigma_0^2 \sum_n z^n(n+1) \right.$$
$$\left. + 3k_3\sigma_0^4 \sum_n z^n(n+1)^2 \right). \tag{14}$$

Using the identities, $\sum_n z^n(n+1) = 1/(1-z)^2$ and $\sum_n z^n(n+1)^2 = (1+z)/(1-z)^3$, and setting $\langle y \rangle = 0$, we obtain from Eq. (14),

$$a = -\frac{3k_3\sigma_0^2}{k}\frac{1+z}{1-z} = -\frac{3k_3}{k}\sigma^2, \tag{15}$$

and hence,

$$\alpha = -\frac{3k_3 k_B}{k^2 r}\frac{z[\ln(z)]^2}{(1-z)^2}. \tag{16}$$

The above proportionality between a and $\sigma^2 = \langle\epsilon\rangle/k$, where $\langle\epsilon\rangle$ is the mean bond energy, implies that the temperature dependence of the thermal expansion a is generally quite different from that of $\sigma^{(3)}/2\sigma^2$ that appears in the classical theories,[4,5] and also that α has the same temperature dependence as the specific heat, $d\langle\epsilon\rangle/dT$. Our expression for a agrees with that of Feynman[7] to leading order in k_3, although our treatments differ. While we use a quasiharmonic approximation, Feynman obtains a by minimizing the free energy $F(a)$. The variational principle can also be used with our approach by minimizing $F \cong F_0 + V(a)$, where $F_0 = k_B T \ln[2\sinh(\hbar\omega/2k_B T)]$, and using the relation $d\omega/da = 3k_3/\mu\omega$ from the Grüneisen parameter, and gives the same result.

The third cumulant may be evaluated similarly:

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$$\sigma^{(3)} = -\frac{2}{Z_0\hbar\omega}\sum_n z^n\left\{(1-z^3)[k_3\sigma_0^6(n+1)(n+2)(n+3)/3] + (1-z)[3k_0 a\sigma_0^4(n+1)^2 + 9k_3\sigma_0^6(n+1)^3]\right\}. \tag{17}$$

Now using $\sum_n z^n(n+1)(n+2)(n+3) = 6/(1-z)^4$ and $\sum_n z^n(n+1)^3 = (1+4z+z^2)/(1-z)^4$, we obtain

$$\sigma^{(3)} = -\frac{k_3(\hbar\omega)^2}{2k^3}\frac{1+10z+z^2}{(1-z)^2}. \tag{18}$$

With the above results, we therefore derive a relation between α and the second and third cumulants which is only a function of T/Θ_E:

$$\frac{\alpha r T\sigma^2}{\sigma^{(3)}} = \frac{3z(1+z)\ln(1/z)}{(1-z)(1+10z+z^2)}. \tag{19}$$

In the next section these results are used to determine high-temperature (HT) and low-temperature (LT) behavior of σ^2, $\sigma^{(3)}$, a, and α.

III. HIGH- AND LOW-TEMPERATURE LIMITS

In the HT limit $z \cong 1 - \hbar\omega/k_B T$, so that

$$a_H \cong -\frac{3k_3}{k^2}k_B T,$$

$$\alpha_H \cong -\frac{3k_3 k_B}{k^2 r},$$

$$\sigma_H^2 \cong \frac{k_B T}{k}, \tag{20}$$

$$\sigma_H^{(3)} \cong -\frac{6k_3}{k^3}(k_B T)^2.$$

Hence we obtain the classical expressions,[3-5] e.g., Eq. (1) and also (see Fig. 2 of Ref. 4) $\Delta r\Delta\sigma^2/\Delta\sigma^{(3)} \cong \Delta T/4T$. These results reflect the proportionality to k_3 of a, α, and $\sigma^{(3)}$ as well as the simple monomial dependence of these quantities on k and T. We emphasize that these results are only valid to first order in k_3 and are simply the first terms in a high-temperature series expansion. The dimensionless small parameter $k_3 a/k$ becomes important only at very high temperatures, $k_B T > k_0^4/(3k_3)^2$, usually well above θ_E.

In the LT limit $z \to 0$, so we can neglect z^2 and higher powers. In this case we obtain

$$a_L \cong -\frac{3k_3}{2k^2}\hbar\omega(1+2z),$$

$$\alpha_L \cong -\frac{3k_3 k_B}{k^2 r}z(\ln z)^2(1+2z),$$

$$\sigma_L^2 \cong \frac{\hbar\omega}{2k}(1+2z), \tag{21}$$

$$\sigma_L^{(3)} \cong -\frac{k_3}{2k^3}(\hbar\omega)^2(1+12z).$$

Note that a, σ^2, and $\sigma^{(3)}$ contain zero point contributions but α vanishes exponentially with Θ_E/T.

IV. EXPERIMENT

XAFS measurements and data analysis were carried out on RbBr at 30 K and 125 K.[8] The second and third cumulants are obtained for both temperatures by fitting theoretical calculations using the *ab initio* XAFS code[9] FEFF5 to data in r-space for the Rb–Br and Rb–Rb bonds, i.e., for first- and second-nearest neighbors, respectively (see Table I).

To calculate the thermal expansion coefficient at each temperature we obtain k and k_3 from fits to Eqs. (20) and then calculate $\omega = \sqrt{k/\mu}$. For the Rb–Rb bond at $T_H = 125$ K, $r = 4.81$ Å, $\mu = M_{\text{Rb}}/2 \approx 7.1 \times 10^{-26}$ Kg, and $\sigma_H^2 = 0.0158$ Å^2, so

$$k = \frac{k_B T_H}{\sigma_H^2} \approx 11\frac{N}{m}, \tag{22}$$

and hence $\omega = 1.24 \times 10^{13}$ Hz. For the low-temperature case $T_L = 30$ K, and hence $w_L = \hbar\omega/k_B T_L \approx 3.14$ and $z_L \approx 0.043$. Using Eqs. (11) and (18) we can now determine σ_L^2 and $\sigma_L^{(3)}$:

$$\sigma_L^2 \cong \frac{\sigma_H^2}{2}\frac{T_L w_L}{T_H}\frac{1+z_L}{1-z_L} \approx 6.5 \times 10^{-3}\text{ Å}^2, \tag{23}$$

$$\sigma_L^{(3)} \cong \frac{\sigma_H^{(3)}}{12}\left[\frac{T_L w_L}{T_H}\right]^2\frac{1+10z_L+z_L^2}{(1-z_L)^2} \approx 5 \times 10^{-5}\text{ Å}^3.$$

Both σ_L^2 and σ_3^L obtained here agree well with experiment (Table I). The thermal expansion coefficient α_H at 125 K can then be obtained from Eq. (1). For α_L at 30 K, we use Eq. (19) with ω determined from a fit to Eqs. (21). This yields

$$\alpha_L = (1.5 \pm 0.6) \times 10^{-5}\text{ K}^{-1},$$
$$\alpha_H = (3.1 \pm 0.3) \times 10^{-5}\text{ K}^{-1}. \tag{24}$$

The two values agree, within uncertainties, with experimental measurements[10] of α. Similar measurements for the nearest-neighbor Rb–Br bond at 30 K and 125 K yield $\alpha_L = (1.1 \pm 0.6) \times 10^{-5}$ K^{-1} and $\alpha_H = (2.9 \pm 0.3) \times$

TABLE I. Cumulants for the Rb–Br and Rb–Rb bonds in RbBr from XAFS experiment at 30 K and 125 K; ω_E is the derived bond Einstein frequency.

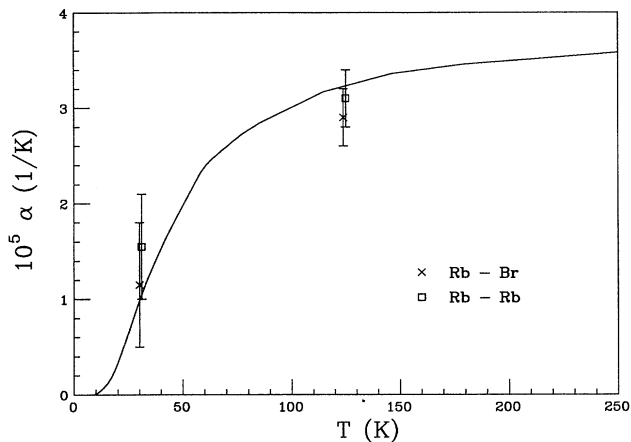| T(K)	Bond	ω_E (10^{13} Hz)	σ^2 (10^{-2} Å^2)	$\sigma^{(3)}$ (10^{-4}Å^3)
30	Rb–Br	1.44 ± 0.05	0.55 ± 0.05	0.28 ± 0.15
30	Rb–Rb	1.17 ± 0.02	0.71 ± 0.05	0.47 ± 0.17
125	Rb–Br	1.52 ± 0.04	1.05 ± 0.05	2.6 ± 0.3
125	Rb–Rb	1.24 ± 0.01	1.58 ± 0.05	6.5 ± 0.2

FIG. 1. Thermal expansion coefficient α in RbBr from experiment (Ref. 10) (solid line) and from this work, for the nearest-neighbor Rb–Br bond (crosses), and the second-neighbor Rb–Rb bond (squares).

10^{-5} K^{-1}, respectively, in agreement with the Rb–Rb results above (see Fig. 1).

V. DISCUSSION AND CONCLUSIONS

We have shown that the fixed classical ratio between the cumulants and the thermal expansion coefficient fails to hold at low temperatures but can be generalized, within the Einstein approximation, in terms of a function only of T/Θ_E. Within the same model, the ther-

mal expansion a and σ^2 are found to be simply proportional at all temperatures. These relations are observed to be in agreement with XAFS experiment in RbBr. These results can also be used to correct for the contribution of $\sigma^{(3)}$ to the XAFS phase and thus eliminate the unphysical contraction with increasing temperature. It is remarkable that a simple anharmonic oscillator model for α agrees to within experimental uncertainty at 30 K. At lower temperatures one expects a power law, rather than an exponential temperature dependence, and also an electronic contribution to the thermal expansion. This agreement is explained in part by the connection in solids[11] between α and the specific heat per unit volume c_v, i.e., $\alpha = \gamma c_v / 3B$ where γ is the Grüneisen parameter and B is the bulk modulus. Since γ and B are nearly temperature independent, $\alpha \propto c_v$, and hence α like c_v is insensitive to details of the vibrational structure.

After this work was completed we learned that equivalent low-temperature formulas for a and $\sigma^{(3)}$ have been derived using a different method by Rabus.[12] Interestingly, Rabus expresses the temperature dependence of $\sigma^{(3)}$ in terms of σ^2; this can also be done here by inverting Eq. (11) to obtain $z = (\sigma^2 - \sigma_0^2)/(\sigma^2 + \sigma_0^2)$.

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