



Review

# By using the anharmonic correlated einstein model to define the expressions of cumulants and thermodynamic parameters in the cubic crystals with new structure factors

Nguyen Ba Duc

Chancellor of Tan Trao University, Tan Trao University, Tuyen Quang City, Vietnam  
Email: hieutruongdhtt@gmail.com, Tel.: +84 273890012

By using potential effective interaction in the anharmonic correlated Einstein model on the basis of quantum statistical theory with phonon interaction procedure, the expressions describing asymmetric component (cumulants) and thermodynamic parameters including the anharmonic effects contributions and by new structural parameters of cubic crystals have been formulated. These new parameters describe the distribution of atoms. The expansion of cumulants and thermodynamic parameters through new structural parameters has been performed. The results of this study show that, developing further the anharmonic correlated Einstein model it obtained a general theory for calculation cumulants and thermodynamic parameters in XAFS theory including anharmonic contributions. The expressions are described through new structural parameters that agree with structural contributions of cubic crystals like face center cubic (fcc), body center cubic (bcc).

**Keywords:** Anharmonic XAFS, cumulants, thermodynamic parameters.

## INTRODUCTION

In the harmonic approximation X-ray Absorption Fine Structure spectra (XAFS), the theoretical calculations are generally well appropriate with the experimental results at low temperatures, because the anharmonic contributions from atomic thermal vibrations may have been neglected. However, at the different high temperatures, the XAFS spectra provide apparently different structural information due to the anharmonic effects, and these effects need to be evaluated. Furthermore, the XAFS spectra at low temperatures may not provide a correct picture of crystal structure. Therefore, this study of the XAFS spectra including the anharmonic effects at high temperatures is crucially needed. The expression of anharmonic XAFS spectra often is described by:

$$\chi(k) = F(k) \frac{\exp[-2R/\lambda(k)]}{kR^2} \text{Im} \left\{ e^{i\Phi(k)} \exp \left[ 2ikR + \sum_n \frac{(2ik)^n}{n!} \sigma^{(n)} \right] \right\}, \quad (1)$$

where  $F(k)$  is the real specific atomic backscattering amplitude,  $\Phi(k)$  is total phase shift of photoelectron,  $k$  is wave number,  $\lambda$  is mean free path of the photoelectron, and  $\sigma^{(n)}$  ( $n = 1, 2, 3, \dots$ ) are the cumulants to describe asymmetric components. They all appear due to the thermal average of the function  $e^{-2ikr}$ , in which the asymmetric terms are expanded in a Taylor series around value  $R = \langle r \rangle$  with  $r$  is instantaneous bond length between absorbing and backscattering atoms at  $T$  temperature and then are rewritten in terms of cumulants.

At first, the cumulant expansion approach has been used mainly fitting the XAFS spectra to extract physical parameters from experimental values. Therefore, some procedure were formulated for the purpose of analytic calculation of cumulants, and the anharmonic correlated Einstein model which has been given results is in

agreement with experimental values. The important development in this procedure is that model has been calculated into the interaction between absorbing and backscattering atoms with neighboring atoms in a cluster of nearest atoms at high temperatures. The potential interaction between the atoms becomes asymmetric due to the anharmonic effects and the asymmetric components were written in terms of the cumulants. The first cumulant is net thermal expansion, the second cumulant is Debye-Waller factor, and the third cumulant is description phase shift of anharmonic XAFS spectra.

Based on the above initial illustration, the main purpose of this work is to formulate the cumulant expressions and write thermodynamic parameters as a general form through the new structure parameters by using the anharmonic correlated Einstein model.

**FOMALISM**

Because the oscillations of a pair single bond between of absorbing and backscattering atoms with masses  $M_1$ ,  $M_2$ , respectively, is affected by neighboring atoms, when taking into account, these effects via an anharmonic correlated Einstein model, effective Einstein potential is formed as follow:

$$U_E(\chi) = U(x) + \dots + \sum_{i=1,2} \sum_{j \neq i} U\left(\frac{\mu}{M_i} \times \hat{R}_{12} \cdot \hat{R}_{ij}\right) \tag{2}$$

where  $\hat{R}$  is the unit bond length vector,  $\mu$  is reduced mass of atomic mass  $M_1$  and  $M_2$ , the sum according to  $i, j$  is the contribution of cluster nearest atoms,  $U(x)$  an effective potential:

$$U(x) \approx \frac{1}{2} k_{\text{eff}} x^2 + k_3 x^3 + \dots, \quad x = r - r_0 \tag{3}$$

where  $r$  is spontaneous bond length between absorbing and backscattering atoms,  $r_0$  is its equilibrium value, and  $k_{\text{eff}}$  is effective spring constant because it includes total contribution of neighboring atoms, and  $k_3$  is cubic anharmonicity parameter which gives an asymmetry in the pair distribution function. The atomic vibration is calculated based on quantum statistical procedure with approximate quasi-harmonic vibration, in which the Hamiltonian of the system is written as harmonic term with respect to the equilibrium at a given temperature plus an anharmonic perturbation, with  $y = x - a$ ,  $a(T) = \langle x \rangle$ ,  $\langle y \rangle = 0$ , we have:

$$H = \frac{P^2}{2\mu} + U_E(\chi) = H_0 + U_E(a) + \delta U_E(y); \quad H_0 = \frac{P^2}{2\mu} + \frac{1}{2} k_{\text{eff}} y^2, \tag{4}$$

with  $a$  is the net thermal expansion,  $y$  is the deviation from the equilibrium value of  $x$  at temperature  $T$ . Next, the use of potential interaction between each pair of atoms in the single bond can be expressed by anharmonic Morse potential for cubic crystals. Expanding to third order around its minimum, we have:

$$U_E(x) = D(e^{-2\alpha x} - 2e^{-\alpha x}) \approx D(-1 + \alpha^2 x^2 - \alpha^3 x^3 + \dots) \tag{5}$$

where  $\alpha$  is expansion thermal parameter,  $D$  is the dissociation energy by  $U(r_0) = -D$ .

From expressions (4), (5) we have potential effective interaction Einstein generalize as:

$$U_E(\chi) = U_E(a) + \frac{1}{2} k_{\text{eff}} y^2 + \delta U_E(y), \quad x = y + a \tag{6}$$

Substituting Eq. (5) into (3) and using Eq. (6) to calculate the second term in Eq. (3) with  $\mu = M/2$  ( $M_1 = M_2 = M$ ), sum of  $i$  is over absorber ( $i = 1$ ) and backscatterer ( $i = 2$ ), and the sum of  $j$  which is over all their near neighbors, excluding the absorber and backscattered themselves, because they contribute in the  $U(x)$ , and calculation of  $(\hat{R}_{12} \cdot \hat{R}_{ij})$  with lattice cubic crystals like s.c, fcc and bcc crystals, we obtain thermodynamic parameters like  $k_{\text{eff}}$ ,  $k_3$  and  $\delta U_E(y)$  in Table 1.

**Table 1.** The expressions of thermodynamic parameters for cubic crystals

Factor	s.c crystal	fcc crystal	bcc crystal
$k_3$	$-5D\alpha^3/4$	$-5D\alpha^3/4$	$-5D\alpha^3/4$
$k_{\text{eff}}$	$3D\alpha^2(1-5\alpha a/4)$	$5D\alpha^2(1-3\alpha a/2)$	$11D\alpha^2(1-45\alpha a/22)/3$
$\delta U_E(y)$	$D\alpha^2(3\alpha y-5\alpha y^3/4)$	$5D\alpha^2(\alpha y-\alpha y^3/4)$	$D\alpha^2(11\alpha y/3-5\alpha y^3/4)$

To compare the above expressions in Table 1, we although see different structures of cubic crystals in which have special common factors, we call these factors as new structure factors  $c_1, c_2$ , the parameters calculated statistically is in Table 2.

**Table 2.** New structural parameters of cubic crystals

Structure	$c_1$	$c_2$
s.c	3	1
fcc	5	6/5
bcc	11/3	18/11

The  $k_3$  parameter is identical with any structures, the expressions of  $k_{\text{eff}}$ ,  $\delta U_E(y)$  thermodynamic parameters for the structural cubic crystals are generalized according to new structural parameters as following forms:

$$k_{\text{eff}} = c_1(D\alpha^2 + c_2ak_3) = \mu\omega_E^2; \quad \delta U_E(y) = D\alpha^2[c_1ay - 5\alpha y^3/4] \quad (7)$$

To derive the analytical formulas for cumulants through new structural parameters for the crystals of cubic structure, we use perturbation theory [5]. The atomic vibration is quantized as phonon, and anharmonicity is the result of phonon interaction. Accordingly, we express  $y$  in terms of annihilation and creation operators  $\hat{a}^+$ ,  $\hat{a}$  respectively:

$$y = \sigma^0(\hat{a} + \hat{a}^+); \quad \sigma^0 = \sqrt{\hbar/2m\omega_E}; \quad \hat{a}^+\hat{a} = n, \quad (8)$$

and use the harmonic oscillator states  $|n\rangle$  as eigenstates with eigenvalues  $E_n = n\hbar\omega_E$ , ignoring the zero-point energy for convenience. The  $\hat{a}^+$ ,  $\hat{a}$  operators satisfy the following properties  $[\hat{a}, \hat{a}^+] = \hat{a}\hat{a}^+ - \hat{a}^+\hat{a} = 1$ ;  $\hat{a}^+|n\rangle = \sqrt{n+1}|n+1\rangle$ ;  $\hat{a}|n\rangle = \sqrt{n}|n-1\rangle$ . The cumulants are calculated by the average value

$$\langle y^m \rangle = \frac{1}{Z} \text{Tr}(\rho y^m), \quad m = 1, 2, 3, \dots, \rho = \exp(-\beta H), \quad \beta = (k_B T)^{-1},$$

where  $Z$  is the canonical partition function,  $\rho$  with  $\beta$  is the statistical density matrix, and  $k_B$  is Boltzmann's constant. The corresponding unperturbed quantities are  $Z_0 = \text{Tr}(\rho_0)$  and  $\rho_0 = \exp(-\beta H_0)$ . To leading order in perturbation  $\delta U_E$ ,  $\rho = \rho_0 + \delta\rho$  with  $\delta\rho$  is given by:

$$\delta\rho = -H\rho\delta\beta; \quad \delta\rho_0 = -H_0\rho_0\delta\beta \quad (9)$$

we obtained:

$$\delta\rho = -\int_0^\beta e^{-\beta H_0} \delta\tilde{U}_E(\beta') d\beta'; \quad \delta\tilde{U}_E(\beta) = e^{\beta H_0} \delta U_E e^{-\beta H_0}.$$

If we put unperturbed quantities equal to zero, we have:

$$Z_0 = \text{Tr} \rho_0 = \sum_n \exp(-n\beta\hbar\omega_E) = \sum_{n=0}^\infty z^n = \frac{1}{1-z},$$

where  $z \equiv e^{-\beta\hbar\omega_E} = e^{-\theta_E/T}$  is the temperature variable and determined by the  $\theta_E = \hbar\omega_E/k_B$  is Einstein temperature. Now we are using above expressions to calculate analytics of the cumulants.

+ *The cumulants even order:*

$$\langle y^m \rangle \Big|_{\text{mch}/2n} \approx \frac{1}{Z} \text{Tr} \rho y^m \approx \frac{1}{Z_0} \text{Tr} \rho_0 y^m = \frac{1}{Z_0} \sum_n e^{-n\beta\hbar\omega_E} \langle n | y^m | n \rangle$$

With  $m = 2$  we have calculation expression of the second cumulant

$$\langle y^2 \rangle = \sigma^{(2)} = \frac{1}{Z_0} \sum_n e^{-n\beta\hbar\omega_E} \langle n | y^2 | n \rangle. \quad (10)$$

Using matrix  $\langle n | y^2 | n \rangle = \langle n | \hat{a}^+\hat{a} + \hat{a}\hat{a}^+ | n \rangle = (\sigma_0)^2(2n+1)$  and substituting into (10) and applying the mathematical transformations, and according to form (7) we have expression of second cumulant which is rewritten through  $c_1$  structural parameter:

$$\sigma^{(2)} = \langle y^2 \rangle = \frac{\hbar\omega_E}{2c_1 D\alpha^2} \frac{(1+z)}{(1-z)}. \quad (11)$$

+ *The cumulants odd order:*

$$\langle y^m \rangle_{\text{mil}} \approx \frac{1}{Z} \text{Tr} \rho y^m \approx \frac{1}{Z_0} \text{Tr} \delta \rho y^m \quad (12)$$

With  $m=1, 3$  we have expression to calculate first cumulant and third cumulant. Transformation following matrix correlative with  $\langle y \rangle$  and  $\langle y^3 \rangle$ , we have:

$$\langle n|y|n+1 \rangle = \sigma_0 \langle n|\hat{a} + \hat{a}^+|n+1 \rangle = \sigma_0 \sqrt{n+1} \langle n|n \rangle = \sigma_0 (n+1)^{1/2}, \quad (13)$$

$$\langle n|y^3|n+1 \rangle = (\sigma_0)^3 (3n\sqrt{n+1} + 3\sqrt{n+1}) \langle n|n \rangle = 3(\sigma_0)^3 (n+1)^{3/2}, \quad (14)$$

$$\langle n|y^3|n+3 \rangle = 3(\sigma_0)^3 [(n+1)(n+2)(n+3)]^{1/2} \quad (15)$$

- The first cumulant ( $m=1$ )

$$\sigma^{(1)} = \langle y \rangle = \frac{1}{Z_0} \sum_{nn'} \frac{e^{-\beta n \hbar \omega_E} - e^{-\beta n' \hbar \omega_E}}{n \hbar \omega_E - n' \hbar \omega_E} \langle n|D[\alpha^2 c_1 a y - \alpha^3 c_3 y^3]|n' \rangle \langle n'|y|n \rangle$$

with  $n'=n+1$  and from Eqs (12, 13) and transform, we have:

$$\langle y \rangle = -\frac{D\alpha^2}{\hbar\omega_E} (\sigma_0)^2 \left[ c_1 a - 3c_3 \alpha (\sigma_0)^2 \frac{(1+z)}{(1-z)} \right] = -\frac{D\alpha^2}{\hbar\omega_E} \frac{\hbar\omega_E}{2k_{\text{eff}}} \left[ c_1 a - 3c_3 \alpha (\sigma_0)^2 \frac{(1+z)}{(1-z)} \right],$$

because  $\langle y \rangle = 0$  and approximate  $k_{\text{eff}} \approx c_1 D\alpha^2$ , the transformation and reduction we obtained first cumulant

$$\sigma^{(1)} = a = \frac{15\hbar\omega_E}{8c_1^2 D\alpha} \frac{(1+z)}{(1-z)} = \frac{15\alpha}{4c_1} \times \sigma^{(2)} \quad (16)$$

- The third cumulant ( $m=3$ )

$$\sigma^{(3)} = \langle y^3 \rangle = \frac{1}{Z_0} \sum_{nn'} \frac{e^{-\beta E_n} - e^{-\beta E_{n'}}}{E_n - E_{n'}} \langle n|\delta U_E|n' \rangle \langle n'|y^3|n \rangle. \quad (17)$$

From Eqs. (7, 17), we have:

$$\langle y^3 \rangle = \frac{D\alpha^2}{Z_0} \sum_{nn'} \frac{e^{-\beta n \hbar \omega_E} - e^{-\beta n' \hbar \omega_E}}{n \hbar \omega_E - n' \hbar \omega_E} \left[ \langle n|c_1 a y|n' \rangle - \langle n|\alpha c_3 y^3|n' \rangle \right] \langle n'|y^3|n \rangle \quad (18)$$

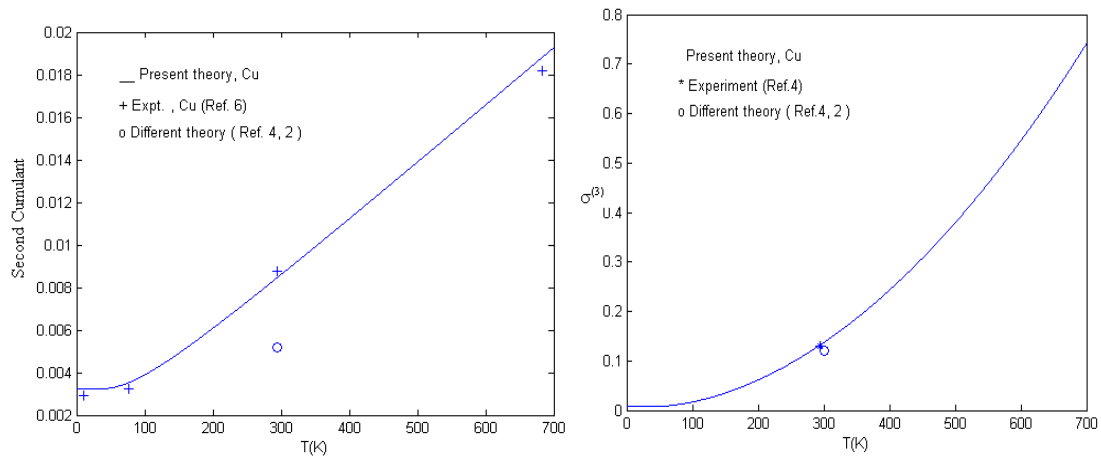
Using Eqs. (14, 15), the calculation of Eq.(18) with  $n'=n+1$ ,  $n'=n+3$ , respectively, and note that matrix only affect  $y^3$  and according to Eqs. (7, 8), we determine the third cumulant:

$$\sigma^{(3)} = \frac{15(\hbar\omega_E)^2}{8c_1^3 D^2 \alpha^3} \frac{(1+10z+z^2)}{(1-z)^2} = \frac{15\hbar\omega_E}{4c_1^2 D\alpha} \frac{(1+10z+z^2)}{1-z^2} \times \sigma^{(2)} \quad (19)$$

The results of the numerical calculations according to present method for cumulants are in agreement with experimental values for Cu crystal (Table 3). The Figures 1 illustrates good agreement of the second, and third cumulants in present theory with experiment values.

**Table 3.** The comparison of the results of  $\sigma^2$  and  $\sigma^{(3)}$  calculated by present theory with experimental data for Cu crystal at different temperatures.

T(K)	$\sigma^2$ (A <sup>2</sup> )		$\sigma^3$ (A <sup>3</sup> )	
	Present	Expt.	Present	Expt.
10	0,00298	0,00292	-	-
77	0,00333	0,00325	0,00010	-
295	0,01858	0,01823	0,000131	0,000130
683	0,01858	0,01823	-	-



**Figure 1.** The graphs illustrate temperature dependence of second (Fig.a) and third (Fig. b) cumulants by present theory and compared to experiment values

## DISCUSSION AND CONCLUSIONS

Developing further the anharmonic correlated Einstein model we obtained a general theory for calculation cumulants and thermodynamic parameters in XAFS theory including anharmonic contributions. The expressions are described through new structural parameters that agree with structural contributions of cubic crystals like face center cubic (fcc), body center cubic (bcc), and results published before [8]. The expression in this work is general case of present procedure when we insert the magnitudes of  $c_1$ ,  $c_2$ , from Table 2 into the calculation of the thermodynamic parameters and above obtained expressions of cumulants. The results of the numerical calculations according to present method for cumulants are in an agreement with experimental values for Cu crystal (Table 3) and illustrated by graphs in Figure 1. This is noted that the experimental values from XAFS spectra are measured at HASYLAB (DESY, Germany).

With the discovery of the XAFS spectra, it provides the number of atoms and the radius of each shell, the XAFS spectroscopy becomes a powerful structural analysis technique. However, the problem still remained to be solved is the distribution of these atoms. The factors  $c_1$ ,  $c_2$ , introduced in the presented work contains the angle between the bond connecting absorber with each atom and the bond between absorber and backscatterer, that is why they can describe the nearest atoms distributions surround absorber and backscatterer atoms. Knowing structure of the crystals and the magnitudes of  $c_1$ ,  $c_2$ , from Table 2 we can calculate the cumulants and then XAFS spectra. But for structure unknown substances we can extract the atomic number from the measured XAFS spectra, as well as, extract the factors  $c_1$ ,  $c_2$ , according to our theory from the measured cumulants like Debye-Waller factor to get information about atomic distribution or structure.

The thermodynamic parameters expressions described by second cumulant or Debye-Waller factor is very convenient, when second cumulant  $\sigma^{(2)}$  is determined, it allows to predict the other cumulants according to Eqs. (21), (24), consequently reducing the numerical calculations and experimental measurements.

## ACKNOWLEDGMENT

The author thanks Prof. Sci. Ph.D Nguyen Van Hung for useful discussions and for authorizing the author to use some results published.

## REFERENCES

- Nguyen QB, Bui BD, Nguyen VH (1999). Statistical Physics, The publisher National University, Hanoi.  
 Beni G, Platzman PM (1976) "Temperature and polarization dependence of extended x-ray absorption fine-structure spectra" *Phys. Rev. B* (14): 1514.  
 Born M, Huang K (1954). *Dynamical Theory of Crystal Lattices* Clarendon Press., Oxford.  
 Crozier, E. D., Rehr, J. J., and Ingalls, R. (1998). *X-ray absorption* edited by D. C. Koningsberger and R. Prins, Wiley New York.  
 Feynman RP (1972). *Statistics Mechanics*, Benjamin, Reading.

Hung NV, Duc NB, Vuong DQ, (2001), "Theory of thermal expansion and cumulants in XAFS technique", *J. Commun. in Phys* (11): 1-9.

Hung NV, Rehr JJ (1997). "Anharmonic correlated Einstein-model Debye-Waller factors" *Phys. Rev. B* (56): 43.

Hung NV, Vu KT, Nguyen BD (2000). "Calculation of thermodynamic parameters of bcc crystals in XAFS theory" *J. Science of VNU Hanoi* (XVI) pp. 11-17.

Accepted 01 September, 2014.

**Citation:** Nguyen Ba Duc (2014). By using the anharmonic correlated einstein model to define the expressions of cumulants and thermodynamic parameters in the cubic crystals with new structure factors. *Journal of Physics and Astronomy Research*, 1(1): 002-006.



**Copyright:** © 2014 Nguyen Ba Duc. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are cited.