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ANALYTIC EQUATION OF STATE FOR GENERALIZED LENNARD-JONES SOLID INCLUDING LOWEST-ORDER ANHARMONIC AND CORRELATION CORRECTIONS*

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Based on the cell model, the general formula for the free energy of solids is derived analytically with the lowest order anharmonic modification and correlation effect taken into account. Combining a method of summing over lattice sites, the analytic equation of state for generalized Lennard-Jones solid is derived. The calculations show that the agreement between theory and computer simulation is quite good and is significantly improved as compared with the numerical results in literature. The comparison of different effects shows the theory including all neighbors but only considering the lowest anharmonic and correlation effects may be a good and convenient approximation for practical solids. The approximation can be easily extended to the quantum case and other generalized potentials.

Keywords: anharmonicity, correlation effect, equation of state, generalized Lennard-Jones system
PACC: 6370, 6410, 6550, 6570

I. INTRODUCTION

The conventional approach to the calculation of the thermodynamic properties of an anharmonic crystal is through Born's theory of lattice dynamics. But the approach has a severe disadvantage, that one cannot get analytic expressions for all thermodynamic quantities, and each elaboration greatly increases the computational requirement. So it is difficult to be used in engineering practice. Lacks and Shuka *et al.*[1,2] have developed a thermodynamic perturbation theory for the nearest-neighbor Lennard-Jones solid. The theory is also fairly complicated and inconvenient for applications. As an alternative, people already developed the free volume theory based on the cell model.

Lennard-Jones and Devonshire (LJD) proposed the free volume theory primarily for Lennard-Jones liquid[3]. The fundamental assumption of the theory is the cell model, which assumes that all molecules of a system are situated in their equilibrium positions except one, which roams near the center of the cell. In the primitive LJD version, the main thermodynamic quantities can be expanded as analytic expressions under anharmonic approximation[4]. But the LJD theory has two disadvantages. The first is the correlation between the motion of various molecules are completely ignored. The second is that the extension of the theory to the generalized Lennard-Jones (GLJ) or other generalized potentials is very difficult.

In fact, the cell model is more in agreement with the practical case of the solid and many works have been done to apply the cell model to solids. Westera and Barker *et al.*[5−7] have proposed a cell-cluster expansion of Ursell-Mayer-type to treat the correlations as a perturbation of some sort. Although the results for the improved theory are in good agreement with the computer simulation results, it is difficult to derive the analytic expressions for the main thermodynamic quantities. And although the LJD theory has been extended to the quantum case[8,9] the extension of the cell-cluster expansion theory to the quantum case is very difficult, so we have no quantum version at present. But the quantum effects and maybe the quantum correlation effects are very important at low temperature. For example, experiments have shown that the Grüneisen parameter tends to zero at low temperature. This is obviously a quantum effect, but no theory can explain it up to now[5]. Otherwise, most of the equations of state for solids are semi-empirical[10−16]; which cannot take any anharmonic or correlation effects into account. Since the complete

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cell-cluster expansion theory is difficult to be applied to the all-neighbors model or other generalized potential systems, the development of practical equations of state for solids in terms of the theory is also a difficult task. This is not enough for practical applications.

A method of summing over the lattice sites is proposed in Ref.[17], by using it the analytic expressions of the main thermodynamic quantities for LJ system was derived easily. Considering the GLJ system is very important as it can be used to describe interactions between a variety of molecules, we would use the method to derive the analytic expressions of the main thermodynamic quantities for the cell-cluster theory. Although the approximate version of the cell-cluster theory only considers the lowest order anharmonic and correlation effects, we can see from the comparison of our results with the complete theory and the computer simulation that such analytic version may be a good and convenient approximation for practical solids. The general formalism in our analytic approximate theory provides not only the possibility to develop practical molecular thermodynamic equations of state for solids but also the possibility to extend the theory to the quantum case. This may lead to a change of the situation that the semi-empirical equations of state being prevalent[10−16], and we expect the quantum correlation effects will be treated properly in due course.

The generalized anharmonic cell model is described in section II. The analytic expressions of the main thermodynamic quantities for GLJ crystal are derived in section III. In section IV, the results for LJ system are compared with the computational simulation and discussed.

II. FUNDAMENTAL FORMULA FOR GENERALIZED ANHARMONIC CELL MODEL

Using the cell model, the total interaction energy for a system can be expressed as[5−7,17]

$$U = U_0 + \sum_{i\neq 0}[u(r_i) - u(0)], \tag{1}$$

where U_0 is the total interaction energy as all molecules are situated at their equilibrium positions, $[u(\boldsymbol{r}_i) - u(0)]$ is the change of potential energy of the i-th molecule when it given a displacement $\boldsymbol{r}_i$ from the equilibrium position.

The free volume is defined as

$$v_f = \int_v \exp\{-[u(\boldsymbol{r}) - u(0)]/kT\}\mathrm{d}\tau. \tag{2}$$

Where v is volume of a cell. The Helmholtz free energy of a molecule can be calculated using the following equation[3]

$$\begin{aligned} f =& \frac{1}{2}u(0) - kT[1 + \ln j(T) \\ &+ \frac{3}{2}\ln\left(\frac{2\pi\mu kT}{h^2}\right) + \ln v_f]. \end{aligned} \tag{3}$$

Supposing the potential function is $\varepsilon(r), u(r)$ can be expressed as

$$u(r) = \sum_{i\neq 0}\varepsilon(|\boldsymbol{R}_i - \boldsymbol{r}|). \tag{4}$$

In usual cases $R_i >> r$ for all i, Eq.(4) can be expanded as series of r

$$\begin{aligned} u(\boldsymbol{r}) =& u(0) + (\boldsymbol{r}\cdot\nabla)u(\boldsymbol{r})|_0 \\ &+ \frac{1}{2}(\boldsymbol{r}\cdot\nabla)^2 u(r)|_0 + \frac{1}{3!}(\boldsymbol{r}\cdot\nabla)^3 u(\boldsymbol{r})|_0 \\ &+ \frac{1}{4!}(\boldsymbol{r}\cdot\nabla)^4 u(\boldsymbol{r})|_0 + \cdots \\ &\approx u(0) + \frac{1}{2}\nabla_r^2 u(r)|_0 \cdot \boldsymbol{r}^2 \\ &+ \frac{1}{6}\nabla_r^3 u(\boldsymbol{r})|_0 \cdot r^3 + \frac{1}{24}\nabla_r^4 u(r)|_0 \cdot r^4. \end{aligned} \tag{5}$$

The second line of Eq.(5) is derived from the consideration that the first order derivative of potential energy equals zero at equilibrium position, and the adoption of spherical symmetry approximation, as well as the omission of higher order terms of r (anharmonic approximation).

Supposing $s = |\boldsymbol{R}_i - r|$, we have $\mathrm{d}s = \mathrm{d}r\cos\theta$, and

$$\begin{aligned} \nabla_r^2 u(r) &= \sum_{i\neq 0}\cos^2\theta\cdot\nabla_s^2\varepsilon(s), \\ \nabla_r^3 u(r) &= \sum_{i\neq 0}\cos^3\theta\cdot\nabla_s^3\varepsilon(s), \\ \nabla_r^4 u(r) &= \sum_{i\neq 0}\cos^4\theta\cdot\nabla_s^4\varepsilon(s), \end{aligned} \tag{6}$$

and where θ is the angle of $\boldsymbol{R}_i$ with $\boldsymbol{r}$. As $u(\boldsymbol{r})$ is highly symmetric for cubic lattices, we take the average for solid angle $\frac{1}{4\pi}\int < \cdots > \mathrm{d}\Omega$, and Eq.(6) can be changed as

$$\begin{aligned} \nabla_r^2 u(r) &= \frac{1}{3}\sum_{i\neq 0}\nabla_s^2\varepsilon(s) = \frac{1}{3}\sum_{i\neq 0}\left[\frac{\partial^2}{\partial s^2} + \frac{2}{s}\frac{\partial}{\partial s}\right]\varepsilon(s), \\ \nabla_r^4 u(r) &= \frac{1}{5}\sum_{i\neq 0}\nabla_s^4\varepsilon(s) = \frac{1}{5}\sum_{i\neq 0}\left[\frac{\partial^2}{\partial s^2} + \frac{2}{s}\frac{\partial}{\partial s}\right]^2\varepsilon(s), \end{aligned} \tag{7}$$

and $\nabla_r^3 u(r) = 0$. It must be pointed out that the derivation of Eq.(7) from Eq.(6) is exact for lattices with cubic symmetries[5], one need not assume the approximation of spherical symmetry for the derivation. Only as Eq.(7) is applied to non-cubic lattices, the derivation becomes an approximation of spherical symmetry.

Substituting Eq.(5) and Eq.(7) into Eq.(3), since the fourth order term can be taken as small, we expand the corresponding exponential function and only keep its first order term to obtain

$$v_f = \int_v \left[1 - \frac{1}{24kT}\nabla_r^4 u(r)|_0 \cdot r^4\right] \cdot \exp\left[-\frac{1}{2kT}\nabla_r^2 u(r)|_0 \cdot r^2\right] 4\pi r^2 \mathrm{d}r, \quad (8)$$

where the integral limit for r is approximately $[0,a/2]$, and a is the distance between nearest neighbors. As the integrated function in Eq.(8) is Gaussian, if the value of the function in the exponent at upper integral limit is larger than some large positive number, the integral limit can be approximately taken as $[0,\infty]$ without influence to the integrated result.
Here we take

$$\frac{1}{2kT}\nabla_r^2 u(r)|_0 \cdot \left(\frac{a}{2}\right)^2 > 6. \quad (9)$$

The formula gives the applicable scope of temperature and density for the model.

On the condition of Eq.(9), evaluating the integral of Eq.(8) and substituting it into Eq.(3), we get

$$f = f_0 + f_1' + f_2' \approx f_0 + f_1 + f_2. \quad (10)$$

Here f_0 is the free energy only taking harmonic approximation[17],

$$f_0 = \frac{1}{2}u(0) - kT\left\{1 + \ln j(T) + \frac{3}{2}\ln\left(\frac{2\pi\mu kT}{h^2}\right) + \frac{3}{2}\ln\left[\frac{2\pi kT}{\nabla_r^2 u(r)|_0}\right]\right\}, \quad (11)$$

f_1' is anharmonic modification to the free energy from Eq.(3) and Eq.(8)

$$f_1' = \frac{5}{32\pi^2}\nabla_r^4 u(r)|_0 \cdot \left[\frac{2\pi kT}{\nabla_r^2 u(r)|_0}\right]^2, \quad (12)$$

and f_2' is the lowest order correlation modification, which can be easily evaluated by using the method in Ref.[5–7]

$$f_2' = -\frac{zkT}{4v_f^2 d^2}\left(\frac{2\pi}{\beta d}\right)^3 (A_1^2 + 2B_1^2), \quad (13)$$

where z is the coordination number of the lattice, and

$$A_1 = \frac{d^2\varepsilon(a)}{da^2}, B_1 = \frac{1}{a}\frac{d\varepsilon(a)}{da}, d = \nabla_r^2 u(r)|_0. \quad (14)$$

Substituting Eq.(8) into Eq.(13), expanding the anharmonic contribution, f_1' and f_2' can be approximately rearranged as f_1 and f_2

$$f_1 = \frac{5}{32\pi^2}\nabla_r^4 u(r)|_0 \cdot \left[\frac{2\pi kT}{\nabla_r^2 u(r)|_0}\right]^2 \cdot \left(1 + \frac{2f_2}{kT}\right), \quad (15)$$

$$f_2 = -\frac{zkT}{4d^2}(A_1^2 + 2B_1^2). \quad (16)$$

Ⅲ. ANHARMONIC OSCILATOR MODEL FOR GLJ CRYSTAL

Now we apply the formula in Section II. to the GLJ system. The GLJ potential is

$$\varepsilon(r) = \frac{\varepsilon_0}{m-n}\left[n\left(\frac{r^*}{r}\right)^m - m\left(\frac{r^*}{r}\right)^n\right]. \quad (17)$$

The expression for $u(0)$ is

$$u(0) = \frac{z\varepsilon_0}{m-n}\left[ns_m\left(\frac{r^*}{a}\right)^m - ms_n\left(\frac{r^*}{a}\right)^n\right] = \Lambda^*\left[A\left(\frac{V^*}{V}\right)^{m/3} - B\left(\frac{V^*}{V}\right)^{n/3}\right], \quad (18)$$

where

$$A = \frac{ns_m}{m-n}, \quad B = \frac{ms_n}{m-n}, \quad (19)$$

$$\Lambda^* = z\varepsilon_0, \quad V^* = (r^*)^3/\gamma, \quad (20)$$

and

$$V = a^3/\gamma. \quad (21)$$

s_m and s_n are structural constants, their values as (or n) being integers can be easily found in Ref.[18]. Yet the value of s_m as m being non-integer is in absence. Here we get an analytic expression of s_m for fcc and bcc structures by fitting the values as m being integers,

$$s_m = 1 - \frac{3.5378}{m^2} + \frac{61.9251}{m^3} + \frac{23923}{m^8} \quad \text{(fcc)}$$
$$s_m = 1 + \frac{21.096}{m^2} + \frac{232.13}{m^4} + \frac{5809.3}{m^6} \quad \text{(bcc)} \quad (22)$$

As the fitting error is less than 0.2%, we postulate that the expressions are also applicable to the case as m being non-integers. The values of structure constant z and γ are given as

$$z = 12 \text{ (fcc)}, 8 \text{ (bcc)},$$
$$\gamma = \sqrt{2} \text{ (fcc)}, \ 3\sqrt{3}/4 \text{ (bcc)}. \quad (23)$$

Combining Eq.(17) with Eq.(7), we get

$$\begin{aligned}\nabla_r^2 u(r)|_0 =&\frac{\varepsilon_0}{3(m-n)(r^*)^2}\sum\left[nm(m-1)\left(\frac{r^*}{R_i}\right)^{m+2}\right.\\&\left.-mn(n-1)\left(\frac{r^*}{R_i}\right)^{n+2}\right]\\=&\frac{z\varepsilon_0}{3(m-n)(r^*)^2}\left[nm(m-1)s_{m+2}\left(\frac{r^*}{a}\right)^{m+2}\right.\\&\left.-mn(n-1)s_{n+2}\left(\frac{r^*}{a}\right)^{n+2}\right],\end{aligned}$$

or

$$\nabla_r^2 u(r)|_0 = \frac{\Lambda^*}{3a^2}\left[C\left(\frac{V^*}{V}\right)^{m/3} - D\left(\frac{V^*}{V}\right)^{n/3}\right]. \tag{24}$$

By the same argument, we get

$$\begin{aligned}\nabla_r^4 u(r)|_0 =&\frac{24\Lambda^*}{5\gamma a V}\left[C_1\left(\frac{V^*}{V}\right)^{m/3}\right.\\&\left.-D_1\left(\frac{V^*}{V}\right)^{n/3}\right],\end{aligned} \tag{25}$$

where

$$\begin{aligned}C &= \frac{mn(m-1)s_{m+2}}{(m-n)},\\D &= \frac{mn(n-1)s_{n+2}}{(m-n)},\\C_1 &= \frac{mn(m^2-1)(m+2)s_{n+4}}{24(m-n)},\\D_1 &= \frac{mn(n^2-1)(n+2)s_{m+4}}{24(m-n)}.\end{aligned} \tag{26}$$

Then Eq.(9) can be changed as

$$T < \frac{\Lambda^*}{144}\left[C\left(\frac{V^*}{V}\right)^{m/3} - D\left(\frac{V^*}{V}\right)^{n/3}\right] \approx \frac{mnz\varepsilon_0}{144k}, \tag{27}$$

where we take the approximations, $V^*/V \sim 1, s_m \sim 1$ and $s_n \sim 1$.

Substituting Eq. (24) and Eq. (25) into Eq. (11) and Eq. (15) respectively, we get

$$\begin{aligned}f_0 =&\frac{\Lambda^*}{2}\left[A\left(\frac{V^*}{V}\right)^{m/3} - B\left(\frac{V^*}{V}\right)^{n/3}\right]\\&-kT\left[1+\ln j(T)+\frac{3}{2}\ln\left(\frac{2\pi\mu kT}{h^2}\right)+\ln(V^*)\right]\\&-kT\ln\left[\gamma\left(\frac{V}{V^*}\right)\right]-\frac{3}{2}kT\ln\left(\frac{6\pi kT}{\Lambda^*}\right)\\&+\frac{3}{2}kT\ln\left[C\left(\frac{V^*}{V}\right)^{m/3} - D\left(\frac{V^*}{V}\right)^{n/3}\right],\end{aligned} \tag{28}$$

$$\begin{aligned}f_1 =&27kT\left(\frac{kT}{\Lambda^*}\right)\frac{\left[C_1\left(\frac{V^*}{V}\right)^{m/3} - D_1\left(\frac{V^*}{V}\right)^{n/3}\right]}{\left[C\left(\frac{V^*}{V}\right)^{m/3} - D\left(\frac{V^*}{V}\right)^{n/3}\right]^2}\\&\cdot\left(1+\frac{2f_2}{kT}\right).\end{aligned} \tag{29}$$

From Eq.(14), Eq.(17) and Eq.(24), Eq.(16) for f_2 can be derived as

$$\begin{aligned}f_2 =&-\frac{9kT}{4z}\left[(m-1)s_{m+2}\left(\frac{V^*}{V}\right)^{m/3}\right.\\&\left.-(n-1)s_{n+2}\left(\frac{V^*}{V}\right)^{n/3}\right]^{-2}\\&\times\left[(m^2+2m+3)\left(\frac{V^*}{V}\right)^{2m/3}\right.\\&-2(mn+m+n+3)\left(\frac{V^*}{V}\right)^{m+n/3}\\&\left.+(n^2+2n+3)\left(\frac{V^*}{V}\right)^{2n/3}\right].\end{aligned} \tag{30}$$

The equation of state can be derived by the thermodynamic relation $P = -\left(\frac{\partial f}{\partial V}\right)_T$. thus

$$\xi = \frac{PV}{kT} = \xi_0 + \xi_1 + \xi_2 \equiv \frac{P_0V}{kT} + \frac{P_1V}{kT} + \frac{P_2V}{kT}, \tag{31}$$

where

$$\begin{aligned}\xi_0 =&\frac{P_0V}{kT} = \frac{\Lambda^*}{6kT}\left[mA\left(\frac{V^*}{V}\right)^{m/3} - nB\left(\frac{V^*}{V}\right)^{n/3}\right]\\&+\frac{\left(\frac{m}{2}+1\right)C\left(\frac{V^*}{V}\right)^{m/3} - \left(\frac{n}{2}+1\right)D\left(\frac{V^*}{V}\right)^{n/3}}{C\left(\frac{V^*}{V}\right)^{m/3} - D\left(\frac{V^*}{V}\right)^{n/3}}\end{aligned} \tag{32}$$

is the pressure under harmonic approximation. For LJ potential, $m = 12$, $n = 6$, the result are in agreement with the LJD free volume theory[4]. Introducing the following auxiliary quantity

$$y = \frac{V^*}{V}, \tag{33}$$

the contribution of f_1 and f_2 to the pressure can be derived as

$$\begin{aligned}\xi_1 =&\frac{P_1V}{kT} = -9\left(\frac{kT}{\Lambda^*}\right)(Cy^{m/3} - Dy^{n/3})^{-3}\\&\cdot\{-6\xi_2(Cy^{m/3} - Dy^{n/3})(C_1y^{m/3} - D_1y^{n/3})\\&+\left(1+\frac{2f_2}{kT}\right)[mCC_1y^{2m/3} - (CD_1(2m-n)\\&+C_1D(2n-m))y^{m+n/3} + nDD_1y^{2n/3}]\},\end{aligned} \tag{34}$$

and

$$\xi_2 = \frac{P_2 V}{kT} = -\frac{3}{z}[(m-1)y^{m/3} - (n-1)y^{n/3}]^{-3} \cdot [(m+2)y^{2m+n/3} + (n+2)y^{m+2n/3}], \quad (35)$$

respectively. For simplicity, we have used in Eq.(34) the approximations $s_m \sim 1$ and $s_n \sim 1$.

IV.RESULTS FOR THE LENNARD-JONES SOLID AND DISSCUSIONS

Using the formalism presented in the previous sections we calculate the thermodynamic properties of the LJ solid. Table I gives the configurational Helmholtz free energy f_P/ε_0 versus reduced density $y = V^*/V$ for three reduced temperatures $\tau = kT/\varepsilon_0$. Here f_P is the total free energy f eliminating second term of f_0 in Eq.(28). Table II gives the reduced pressure PV^*/ε_0 versus density for the same temperatures. In the two tables, we compared the contributions of different effects to the free energy and pressure. It is shown that even the harmonic approximation can give fairly good results. The results including the lowest-order anharmonic and correlation corrections are in best agreement with Monte Carlo computer simulation[19], and are significantly improved as compared with the numerical results of Cottin and Monson using the complete version of cell-cluster theory including first-order correlation correction and all anharmonic effects[20]. The two tables also show that the results obtained by ignoring the contributions of non-nearest neighbors to the thermal parts of free energy and pressure are almost in agreement with the original; however, the difference introduced by completely ignoring the contributions of non-nearest neighbors in both the thermal and cold parts is fairly large. So the contributions of non-nearest neighbors to the thermodynamic quantities are mainly the contributions to the cold parts, and the ignorance of the contributions to the thermal parts is a good approximation.

Table 1. The configuration free energy (f_P/ε_0) of the LJ solid versus reduced density ($y = V^*/V$) at three temperatures ($\tau = kT/\varepsilon_0$). M, simulation. C, Cottin and Monson. S, this paper: S0, harmonic approximation; S1–S3, anharmonic approximation including correlation effects; S1, including all-neighbors; S2, including all-neighbors only in the cold part; S3, nearest-neighbor approximation.

τ	y	1.1	1.15	1.2	1.25
0.75	M	–3.75	–3.41	–2.87	–2.21
	C	–3.57	–3.24	–2.72	–2.03
	S0	–3.62	–3.23	–2.68	–1.96
	S1	–3.72	–3.34	–2.81	–2.10
	S2	–3.69	–3.32	–2.79	–2.09
	S3	–0.82	–0.19	0.61	1.59
1.35	M	–0.93	–0.43	0.21	0.98
	C	–0.72	–0.16	0.50	1.36
	S0	–0.82	–0.19	0.57	1.50
	S1	–0.90	–0.33	0.39	1.28
	S2	–0.86	–0.29	0.43	1.31
	S3	2.02	2.84	3.82	4.99
2.74	M	4.20	5.24	6.35	7.74
	C	4.75	5.72	6.82	8.14
	S0	4.29	5.46	6.74	8.14
	S1	4.58	5.51	6.62	7.90
	S2	4.65	5.58	6.68	7.96
	S3	7.52	8.71	10.1	11.6

Table 2. The reduced pressure (PV^*/ε_0) of LJ solid versus reduced density ($y = V^*/V$) at three temperatures ($\tau = kT/\varepsilon_0$). M, simulation. C, Cottin and Monson. S, this paper: S0, harmonic approximation; S1–S3, anharmonic approximation including correlation effects; S1, including all-neighbors; S2, including all-neighbors only in the cold part; S3, nearest-neighbor approximation.

τ	y	1.1	1.15	1.2	1.25
0.75	M	7.55	11.9	17.6	24.9
	C	7.24	11.7	17.6	25.1
	S0	8.00	12.3	18.1	25.4
	S1	7.39	11.9	17.7	25.1
	S2	7.45	11.9	17.6	25.0
	S3	13.4	18.7	25.5	33.8
1.35	M	12.5	17.1	23.1	30.7
	C	12.0	16.7	22.9	30.4
	S0	13.9	18.4	24.2	31.7
	S1	12.1	17.0	23.1	30.8
	S2	12.9	17.5	23.4	30.9
	S3	18.1	23.8	30.9	39.5
2.74	M	23.6	28.8	35.0	43.2
	C	22.1	27.6	34.4	42.8
	S0	27.6	32.3	38.4	46.2
	S1	20.5	27.0	34.3	42.9
	S2	25.7	30.5	36.7	44.6
	S3	26.7	33.9	40.2	51.5

Here we should point out that the second-order correlation effect is smaller than the contribution of non-nearest neighbors to the thermal parts, so its ignorance is also a reasonable approximation. Westera and Cowly[5] have shown the contribution of second-order correlation effects to the free energy is approximately

$$f_{c2} \approx -6 \times 0.00712kT = -0.04272kT.$$

We can easily estimate the difference of the thermal part of free energy with and without the contributions of the non–nearest neighbors as follows

$$f_d \approx \frac{3}{2}kT[\ln(132.6y^2 - 63.6) - \ln(132y^2 - 60)].$$

Here we ignored the difference of anharmonic and correlation parts, although it is obvious that the two parts may enlarge the difference f_d. The value of y can be estimated by its value at zero temperature, $y^2 \approx \frac{1}{2}(2.409/1.011) \approx 1.1914$. Then the value of f_d can be estimated as

$$f_d \approx -0.0445kT.$$

So it has been shown that absolute value of f_{c2} is indeed smaller than that of f_d. Since the ignorance of f_d is a good approximation, the same is for f_{c2}; or one can include the contribution of non-nearest neighbors, but ignore the second-order correlation effects for the simplicity of the former and the complication of the latter.

Our analytic approximate theory can be easily extended to the quantum case with the quantum correlation effects taken into account, which no existing theory can access, including the quantum cell model and the Monte Carlo or molecular dynamic simulation[5]. It is well known that the quantum effects are not negligible at very low temperature. For example, the experimental results in Ref.[5] shows the Grüneisen parameter tends to zero at low temperature, this is obviously a quantum effect, and most possiblely a quantum correlation effect, but no existing theory can explain it up to now. Now we have developed a method to extend the analytic approximate theory to the quantum case, the results obtained are encouraging and will be published elsewhere. On the other hand, Vinet *et al.*[12] have pointed out that a classical theory is applicable when the temperature is higher than the Debye temperature Θ_D. So the theory in this paper also can be applied to other more general potentials, such as in the case Ref.[21], when an important generalized potential is advanced as

$$\varepsilon(r) = \varepsilon_0 \left[A \left(\frac{r_e}{r}\right)^m e^{-\alpha r/r_e} - B \left(\frac{r_e}{r}\right)^n e^{-\beta r/r_e}\right],$$

$$A = \frac{(n+\beta)}{(m+\alpha-n-\beta)}e^{\alpha}, \quad B = \frac{(m+\alpha)}{(m+\alpha-n-\beta)}e^{\beta},$$

Here ε_0, r_e, m, n, α and β are six independent parameters for the potential. It is obvious that the generalized potential can be changed to the GLJ potential as $\alpha = 0$, and $\beta = 0$, the Morse potential as $m = 0$, $n = 0$ and $\alpha = 2\beta$, the Exp-6 potential as $m = 0$, $\beta = 0$ and $n = 6$, respectively. Although the generalized potential is more complicated than the GLJ potential, the formula in Section II also can be directly applied to the potential, and the expressions for main thermodynamic quantities can be derived analytically. However, the application of the complete cell-cluster expansion theory to the generalized potential is unimaginable.

V. CONCLUSIONS

Using a method of summing over lattice sites, we developed an analytic expression of free energy for generalized Lennard-Jones solid within the frame of the cell model. The expression has taken the lowest-order anharmonic modification and correlation effect into account. The equation of state is analytically derived including the lowest-order anharmonic modification and correlation effects. The comparison of different effects shows the contribution of the non-nearest neighbors to the cold parts of thermodynamic quantities must be taken into account, while the contribution to the thermal parts is negligible, and the contribution of the second-order correlation effect is also negligible. The theory including all neighbors but only considering the lowest-order anharmonic and correlation effects may be a good and convenient approximation to the practical solids. The analytic approximate formula developed here can be easily extended to the quantum case and other generalized potentials.

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