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Calculation of three-body dispersive energies: Extrapolation method and application to crystals of isotropic and anisotropic bodies

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A fast and accurate extrapolation method for the calculation of three-body dispersive forces in crystals is presented. The method is checked against high-precision results for the fcc, bcc, sc, and hcp lattices, and results for the diamond lattice are presented. The effects of anisotropy and molecular orientation are studied using the *Pa*3 and *Cmca* structures as examples, and it is found that the three-body energy is not very sensitive to these parameters. Calculations for the crystals of chlorine, nitrogen, and α- and β-acetylene are performed, and it is found that in some cases the three-body dispersive energy amounts to nearly 15% of the packing energy.

I. INTRODUCTION

It has been well established that the three-body dispersive energy gives an important contribution to the total energy of rare-gas crystals.[1,2] The leading term (dipole-dipole-dipole interaction) has been calculated with great accuracy for the fcc, bcc, sc, and hcp structures;[1,3,4] most published calculations deal with thermodynamical and elastic properties of the rare gases, both in the solid[5] and liquid state,[6] and of mixtures of them,[7] that is, the interacting bodies have spherical symmetry and therefore isotropic polarizabilities.

In contrast, very few calculations of the three-body energy of anisotropic bodies have been performed. Stogryn,[8] for instance, studied the effect of anisotropy and relative orientation for one triplet of a particular geometry, and Monson and Rigby[9] performed calculations on a fcc lattice containing axially symmetric molecules, using the results to estimate the associated nonadditive energy of α-N_2 and CO_2.

The calculation is, in general, cumbersome: The method commonly used, which consists in taking into account triplet interactions within a sufficiently large sphere, shows a very slow convergence and it is necessary to take account of a very large number of terms to achieve reasonable accuracy.[1] For anisotropic bodies, moreover, the corresponding expressions become quite more complicated than the well-known Axilrod-Teller[10] formula for interactions between spherical bodies.

In the present work we propose a method which allows the fast and accurate calculation of the three-body dispersive energy for isotropic and anisotropic bodies. The approximation is checked against high-accuracy available results for the fcc, bcc, sc, and hcp lattices and extended to the diamond structure. The effect of anisotropy and molecular orientation is evaluated on two structures with underlying fcc lattice, *Cmca* and *Pa*3. Finally, calculations on the real crystals Cl_2, α-N_2, and α- and β-acetylene are performed.

II. THEORY

The energy of a system of N bodies due to pairwise interactions W_{ab} between bodies a and b is

$$W_2^{(N)}=\frac{1}{2}\sum_{a=1}^{N}\sum_{b=1}^{N}{}' W_{ab} , \tag{1a}$$

where the prime indicates that $a\neq b$. In a crystal, use of translational symmetry and periodic boundary conditions leads to the expression of the energy associated with an arbitrary origin body 1:

$$W_2^{(1)}=\frac{1}{2}\sum_{b>1}^{N} W_{1b} . \tag{1b}$$

Similarly, the nonadditive three-body energy between bodies a, b, c, and the corresponding energy associated with body 1 is written as

$$W_3^{(N)}=\frac{1}{6}\sum_{a=1}^{N}\sum_{b=1}^{N}{}'\sum_{c=1}^{N}{}'' W_{abc} , \tag{2a}$$

$$\begin{aligned} W_3^{(1)}&=\frac{1}{6}\sum_{b>1}^{N}\sum_{c>1}^{N}{}' W_{1bc} \\ &=\frac{1}{3}\sum_{b>1}^{N-1}\sum_{c(>b)}^{N} W_{1bc} , \end{aligned} \tag{2b}$$

where the primes in (2a) indicate that $a\neq b\neq c$, and in (2b) that $b\neq c$.

A. Dipolar dispersive energies

We are interested, in particular, in the calculation of dipolar dispersive energies. General expressions may be worked out using the Rayleigh-Schrödinger perturbation theory up to third order (see Refs. 1 and 11); however these "exact" expressions cannot be used directly because of our incomplete knowledge of the transition moments and self-energies involved. A usual approximation,[8,9] proposed by Buckingham,[12] is to write

$$W_{ab}=-\tfrac{1}{6}C_{ab}g_{ab} \ , \tag{3a}$$

$$W_{abc}=\tfrac{1}{3}\nu_{abc}g_{abc} \ . \tag{3b}$$

If a, b, and c are identical bodies,

$$g_{ab}=\boldsymbol{\alpha}_a^*\boldsymbol{\alpha}_b^*\mathbf{T}_{ab}^{(2)}\mathbf{T}_{ab}^{(2)} \ , \tag{4a}$$

$$g_{abc}=\boldsymbol{\alpha}_a^*\boldsymbol{\alpha}_b^*\boldsymbol{\alpha}_c^*\mathbf{T}_{ab}^{(2)}\mathbf{T}_{bc}^{(2)}\mathbf{T}_{ca}^{(2)} \ , \tag{4b}$$

$$C_{ab}=C=\tfrac{3}{4}U\alpha^2 \ , \tag{4c}$$

$$\nu_{abc}=\nu=\tfrac{3}{4}\alpha C \ , \tag{4d}$$

where $\boldsymbol{\alpha}_a$ is the static dipolar polarizability; $\alpha_a=\frac{1}{3}\mathrm{Tr}(\boldsymbol{\alpha}_a)$, $\boldsymbol{\alpha}_a^*=\boldsymbol{\alpha}_a/\alpha_a$, $\mathbf{T}_{ab}^{(2)}$ is the second-order interaction tensor $-\nabla^2(1/R_{ab})$, with R_{ab} the distance between bodies a and b, and U is a "characteristic energy" of the body.

It can be seen that the dispersive energies are the product of an "intensity factor" (C,ν) and a "geometrical factor" (g). Strictly speaking, g also contains, besides the information on relative positions and orientations of the bodies, information about their symmetry and shape, via the tensors $\boldsymbol{\alpha}^*$. In the case of spherical bodies, however, $(\boldsymbol{\alpha}^*)_{ij}=\delta_{ij}$, and g_{ab} and g_{abc} are strictly geometrical factors, as defined by Bell.[1]

B. Geometrical factors

Writing out explicitly $\mathbf{T}_{ab}^{(2)}$, the geometrical factors [Eqs. (4a) and (4b)] may be written as

$$g_{ab}=[9(\boldsymbol{\alpha}_a^*)_{ij}(\boldsymbol{\alpha}_b^*)_{kl}r_i^{ab}r_j^{ab}r_k^{ab}r_l^{ab}-6(\boldsymbol{\alpha}_a^*)_{ij}(\boldsymbol{\alpha}_b^*)_{jk}r_i^{ab}r_k^{ab}+(\boldsymbol{\alpha}_a^*)_{ij}(\boldsymbol{\alpha}_b^*)_{ji}]R_{ab}^{-6} \ , \tag{5}$$

$$\begin{aligned} g_{abc}=-\Bigg\{&27(\boldsymbol{\alpha}_a^*)_{ij}(\boldsymbol{\alpha}_b^*)_{kl}(\boldsymbol{\alpha}_c^*)_{mn}r_j^{ab}r_k^{ab}r_l^{bc}r_m^{bc}r_n^{ca}r_i^{ca}-9\sum_{\mathrm{p}}[(\boldsymbol{\alpha}_a^*)_{ij}(\boldsymbol{\alpha}_b^*)_{ik}(\boldsymbol{\alpha}_c^*)_{lm}r_k^{bc}r_l^{bc}r_m^{ca}r_j^{ca}] \\ &+3\sum_{\mathrm{p}}[(\boldsymbol{\alpha}_a^*)_{ij}(\boldsymbol{\alpha}_b^*)_{kl}(\boldsymbol{\alpha}_c^*)_{jl}r_i^{ab}r_k^{ab}]-(\boldsymbol{\alpha}_a^*)_{ij}(\boldsymbol{\alpha}_b^*)_{jk}(\boldsymbol{\alpha}_c^*)_{ki}\Bigg\}R_{ab}^{-3}R_{bc}^{-3}R_{ca}^{-3} \ , \end{aligned} \tag{6}$$

where $i,j,\ldots,$ label Cartesian components, and $\sum_{\mathrm{p}}$ indicates the sum of the three terms obtained by cyclic permutation of a, b, and c. For cylindrical symmetry it is useful to define $\alpha_{\parallel}$ and $\alpha_{\perp}$ as the diagonal polarizability tensor components, parallel and perpendicular to the unique axis of the body, $\hat{\mathbf{n}}$; in this case it is easy to verify that

$$(\boldsymbol{\alpha}^*)_{ij}=(1-K)\delta_{ij}+3Kn_in_j \ , \tag{7a}$$

with

$$K=(\alpha_{\parallel}-\alpha_{\perp})/\mathrm{Tr}(\boldsymbol{\alpha}) \ , \tag{7b}$$

and Eq. (5) reduces to the form used by de Boer.[13]

For spherical bodies, $(\alpha^*)_{ij}=\delta_{ij}$ and $g_{ab}=6R_{ab}^{-6}$, and the well-known form $W_{ab}=-C_{ab}R_{ab}^{-6}$ for the induced-dipole–induced-dipole interaction is obtained.

Also for spherical bodies, the geometrical factor for the three-body interaction [Eq. (6)] is

$$\begin{aligned} g_{abc}&=[27c_ac_bc_c+9(c_a^2+c_b^2+c_c^2)-6]R_{ab}^{-3}R_{bc}^{-3}R_{ca}^{-3} \\ &=3(1+3c_ac_bc_c)R_{ab}^{-3}R_{bc}^{-3}R_{ca}^{-3} \ , \end{aligned} \tag{8}$$

where c_a, c_b, and c_c, are the cosines of the internal angles of the triangle with vertices at the bodies a, b, and c. Equation (8) is identical with that reported by Bell,[1] and leads to the well-known Axilrod-Teller[10] and Muto[14] expression for W_{abc}.

III. CALCULATION METHOD

According to Eqs. (1)–(4), for a crystal of identical bodies the two- and three-body dispersive energy per body is written as

$$W_2^{(1)}=-\tfrac{1}{12}CG_2 \ , \tag{9a}$$

$$W_3^{(1)}=\tfrac{1}{9}\nu G_3 \ , \tag{9b}$$

with

$$G_2=\sum_{b>1}^{N}g_{1b} \ , \tag{10a}$$

$$G_3=\sum_{b>1}^{N-1}\sum_{c(>b)}^{N}g_{1bc} \ . \tag{10b}$$

In this section we deal with two problems connected with the numerical calculation of the geometrical factors of a crystal, the practical limits for the evaluation of the sums in Eqs. (10) and the corresponding extrapolation methods to take account of the infinite crystal, and the use of symmetry considerations to reduce the computational work.

A. Extrapolation method and triplet selection

In the simple case of pairwise interactions a straightforward extrapolation method has been shown to be extremely efficient.[15] In short, we take an "interaction radius" R_i which defines a sphere around the central body, and write

$$G_2=G_2(\infty)=G_2(R_i)+\Delta G_2(R_i) \ , \tag{11a}$$

where

$$G_2(R_i)=\sum_{R_{1b}(\leq R_i)}g_{1b}(R_{1b}) \ , \tag{11b}$$

$$G_2(R_i)=\sum_{R_{1b}(>R_i)}g_{1b}(R_{1b}) \ . \tag{11c}$$

Equation (11a) is exact by definition, whereas $G_2(R_i)$ yields an approximate value of $G_2(\infty)$, obtained by considering $N_2(R_i)$ interactions; $N_2(R_i)$ is proportional to R_i^3.

The simplest estimation of $\Delta G_2(R_i)$ consists in supposing a uniform distribution of bodies b over the space defined by $R_{1b}>R_i$:

$$\Delta G_2(R_i) \simeq \iiint_{(R_{1b}>R_i)} \rho g_{1b}(R_{1b}) d^3V_b \,, \tag{12}$$

where ρ is the "body density" in the crystal [Z/(cell volume)]. In the case of dispersive energies of isotropic bodies, $g_{1b}=6R_{1b}^{-6}$, and

$$\Delta G_2(R_i) \simeq 8\pi\rho R_i^{-3} \,. \tag{13}$$

In Eq. (11a) it can be seen that $\Delta G_2(R_i)$ varies continuously with R_i, while $G_2(R_i)$ changes stepwise each time R_i reaches a shell of bodies; in truth, to be consistent, the density of bodies within the interaction sphere should be that of the crystal. Therefore we define R_i by

$$\tfrac{4}{3}\pi\rho R_i^3 = N_2(R_i)+1 \,, \tag{14}$$

which gives one solution R_i for each possible value of $N_2(R_i)$.

The same formula [Eq. (13)] may be used for anisotropic bodies: In this case, however, the additional assumption of a uniform distribution of the orientations of the bodies is made, and for large anisotropies the approximation is expected to be somewhat less accurate. Numerical examples will be given in Sec. IV B.

Things are more complicated for three-body interactions. Usually, by similarity with the two-body case, the geometrical factor is approximated by

$$G_3^*(R_i) = \frac{1}{2} \sum_{\substack{b,c(>1)\\ R_{1b}(\le R_i)\\ R_{c1}(\le R_i)}}{}' g_{1bc} = \sum_{\substack{b,c(c>b>1)\\ R_{1b}(\le R_i)\\ R_{c1}(\le R_i)}} g_{1bc} \,, \tag{15}$$

that is, all triplets containing the central body, within a sphere of radius R_i, are taken into account. Although for the limiting case $R_i \to \infty$ the result will be obviously correct, the convergence of $G_3^*(R_i)$ to its limit $G_3(\infty)$, which has been well studied for the fcc and hcp structures,[1] is extremely slow, with the additional problem that the number of triplets grows as R_i^6. This slow convergence is partly due, in our opinion, to the fact that the calculation of $G_3^*(R_i)$ as described above is, to a certain extent, inconsistent. In Fig. 1 we show some examples of this inconsistency. Of the six triangles with one vertex at the center of the circle of radius R_i, only the isosceles triangle shown in full lines is included in $G_3^*(R_i)$. The other two isosceles triangles, which are identical by translational symmetry, will only be counted when R_i is increased from about 4.5 to 6 nearest-neighbor distances. Furthermore, in the isotropic case [Eq. (8)], the other three triangles, also omitted in $G_3^*(R_i)$, each contribute $\sim$76 times more to $G_3(\infty)$ than the isosceles triangle. In conclusion, by summing triplets over a sphere many weak interactions are calculated, and many large ones are omitted for finite values of R_i. The optimal way of performing the sum would be to take equipotential surfaces defined by Eq. (8), but this is complicated by the presence of the angular factor $A=1+3c_ac_bc_c$. However, A varies between the limits -2 and $\frac{11}{8}$, and a practical approximation to the problem is to take into account the largely varying factor $R_{1b}^{-3}R_{bc}^{-3}R_{c1}^{-3}$.

For a given R_i, the set of values of (R_{1b},R_{bc},R_{c1}) may be decomposed in eight disjoint subsets (S_{1b},S_{bc},S_{c1}) defined as $S_{km}=T$ if $R_{km}\le R_i$; $S_{km}=F$ if $R_{km}>R_i$ $(k,m=1,b,c)$. Equation (10b) may then be written as

$$\begin{aligned} G_3 = G_3(\infty) = {} & G_{TTT}(R_i) \\ & + [G_{TTF}(R_i)+G_{TFT}(R_i)+G_{FTT}(R_i)] \\ & + [G_{TFF}(R_i)+G_{FTF}(R_i)+G_{FFT}(R_i)] \\ & + G_{FFF}(R_i) \,. \end{aligned} \tag{16}$$

The different regions of space thus defined are depicted in Fig. 2. Figure 2(a) corresponds to the case $S_{1b}=T$ and Fig. 2(b) to $S_{1b}=F$. Note that the region FTT disappears if $R_{1b}>2R_i$.

It can be seen that

$$G_3^*(R_i) = G_{TTT}(R_i) + G_{TFT}(R_i) \,. \tag{17}$$

However, by translational symmetry, every term $g_{1bc} \in G_{TFT}$ will give rise to identical terms in G_{TTF} and G_{FTT} (see Fig. 1). Therefore

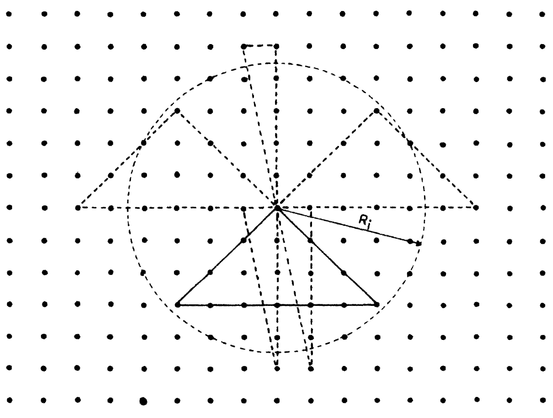

FIG. 1. Triangles indicate triplet interactions in a square lattice. Only the triangle drawn in solid lines lies within the circle, and is counted in G_3^* (see text).

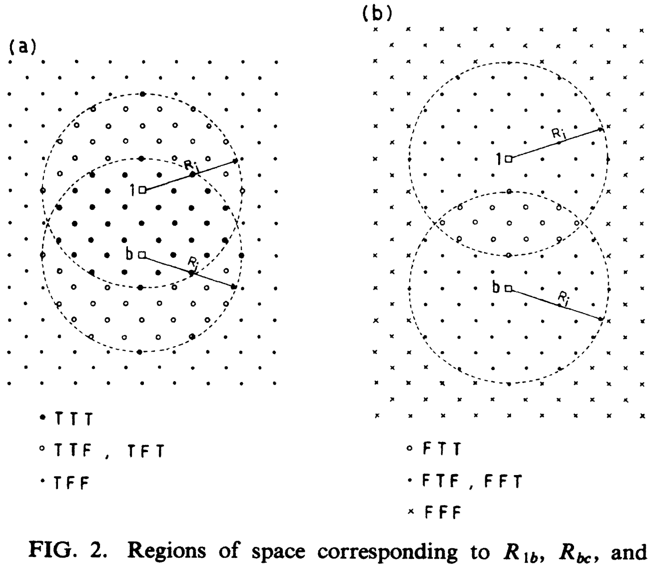

FIG. 2. Regions of space corresponding to R_{1b}, R_{bc}, and $R_{c1} \gtrless R_i$. (a) $R_{1b}\le R_i(T)$; (b) $R_{1b}>R_i(F)$.

$$G_{TFT}(R_i)=G_{TTF}(R_i)=G_{FTT}(R_i)$$

and similarly

$$G_{TFF}(R_i)=G_{FTF}(R_i)=G_{FFT}(R_i)\ .$$

Therefore, the exact value G_3 given by Eq. (16) may be expressed in the form

$$G_3(\infty)=G_3(R_i)+\Delta G_3(R_i)\ , \tag{18a}$$

with

$$G_3(R_i)=G_{TTT}(R_i)+3G_{TFT}(R_i)\ , \tag{18b}$$

$$\Delta G_3(R_i)=3G_{TFF}(R_i)+G_{FFF}(R_i)\ . \tag{18c}$$

In the regions *TTT* and *TFT*, every body in a triplet lies at a distance smaller than R_i of at least one other body. On the contrary, in the regions *TFF* and *FFF* at least one body lies at distances larger than R_i from the other two components of the triplet. For a given value of R_i, there are a finite number of terms in G_{TTT} and G_{TFT}; these are evaluated explicitly. G_{TFF} and G_{FFF} contain an infinite number of terms, and must be approximated.

For G_{TFF} we may assume that the *c* bodies are uniformly distributed in space, by analogy with the case of pairwise interactions. With this approximation

$$\begin{aligned} G_{TFF}(R_i) &\simeq \tfrac{1}{2} \sum_{R_{1b}(\leq R_i)} \iiint_{(R_{bc},R_{c1}>R_i)} \rho g_{1bc} d^3V_c \\ &= (\pi\rho/8R_i^6) \sum_{R_{1b}(\leq R_i)} (6R_i^2 R_{1b}^{-2}-1)\ . \end{aligned} \tag{19}$$

Similarly, G_{FFF} may be approximated by assuming uniform distributions of both bodies *b* and *c* in the corresponding region, and we may write

$$\begin{aligned} G_{FFF}(R_i) &\simeq \tfrac{1}{2} \iiint \iiint_{(R_{1b},R_{bc}\ R_{c1}>R_i)} \rho^2 g_{1bc} d^3V_b d^3V_c \\ &= 5\pi^2\rho^2/2R_i^3\ . \end{aligned} \tag{20}$$

Again, the value of R_i is chosen as in the pairwise interaction, Eq. (14). The approximations (19) and (20) may be used also for the anisotropic case, with the same limitations as in the two-body case. In Sec. III A we will show numerical results of this approximation.

B. Symmetry considerations

In addition to the reduction in computing time and the corresponding increase in accuracy which can be obtained by the use of the extrapolation formulas, symmetry considerations allow further simplification of the calculations. The sphere $R \leq R_i$ defines a finite atomic cluster; the symmetry of the finite cluster is identical with the site symmetry of the central atom of the sphere in the (infinite) crystal; in many cases it coincides with the full factor group symmetry.

The position of one atom in the cluster defines geometrically a pairwise interaction with the central atom. Likewise the positions of two atoms define a triplet with the central atom for a three-body interaction; the cluster will in almost all cases have other atoms (pairs of atoms) which are equivalent by symmetry, and it is obviously advantageous to perform each calculation only on pairs and triplets which are not equivalent by symmetry. It is straightforward to see that this problem is fully equivalent to that of finding the nonequivalent configurations of finite clusters containing one and two substitutional impurities, respectively. The general case of clusters with substitutional impurities has been dealt with in a recent paper.[16] The one-impurity problem is very simple, and the two-impurity problem may be solved by using a method based on a double coset decomposition of the group of the cluster with respect to its subgroups. This use of symmetry properties allows a sizable reduction of the computing time. The number of equivalent configurations is given by the ratio of the dimension of the group of the cluster, $|G|$, and that of the subgroup of the configuration; since most configurations in relatively large clusters have trivial (C_1) symmetry, this factor is not far from $|G|$. Therefore the method is most useful for high-symmetry structures.

IV. RESULTS

A. Isotropic bodies: fcc, bcc, sc, hcp, and diamond structures

For these structures, G_2 and G_3 depend only on one lattice parameter. In order to study the convergence of the proposed approximation method, we have calculated G_2 and G_3 for different values of $R_i = xR_0$, where R_0 is the nearest-neighbor distance, in the range $1 \leq x \leq 3$; these calculations may be then compared with the "limiting value," obtained from a calculation with $x=5$. Table I contains the limiting values obtained, the corresponding numbers of pairs N_2 and triplets $N_3 = N_2\ (N_2-1)/2$ included in the calculation of $G_2(R_i)$ and $G_3(R_i)$, the numbers of symmetry independent pairs and triplets $\mathcal{N}_2$ and $\mathcal{N}_3$ (as described in Sec. III B) and the partial contributions $G_2(R_i)$, $\Delta G_2(R_i)$, $G_{TTT}(R_i)$, $G_{TFT}(R_i)$, $G_3(R_i)$, and $\Delta G_3(R_i)$.

Let us analyze the result for the fcc structure in some detail. The limiting value of the three-body interaction of 7.633 928 may be compared with that reported by Bell;[1] he used $N_3 = 4\,661\,931$, obtaining $G_3^* = 7.620\,56$. Bell also reports an extrapolated value of 7.629 33, and a high-precision calculation by Huller[3] yields 7.629 965. On the other hand, our values for G_2 differ from those reported by Hirschfelder[17] by less than 1 in 10^6.

The advantages of the use of symmetry are also clearly seen. The ratio $N_2/\mathcal{N}_2$ is about 24, since many single bodies lie at sites of high symmetry; however, $N_3/\mathcal{N}_3$ is about 44, close to $|G|=48$, because most triplets (or pairs of bodies excluding the central one) have C_1 symmetry. The reduction is also apparent for the other structures; $N_3/\mathcal{N}_3$ is about 41 for the bcc and sc structures, whereas for diamond ($|G|=24$) it is about 21. Of course, these numbers depend in each case on the value of x employed in the calculation.

Figure 3 shows the convergence of $G_2(R_i)$, G_2, $G_3^*(R_i)$, and G_3 to their limiting values, as a function of x and N_2, for the structures under consideration. For the

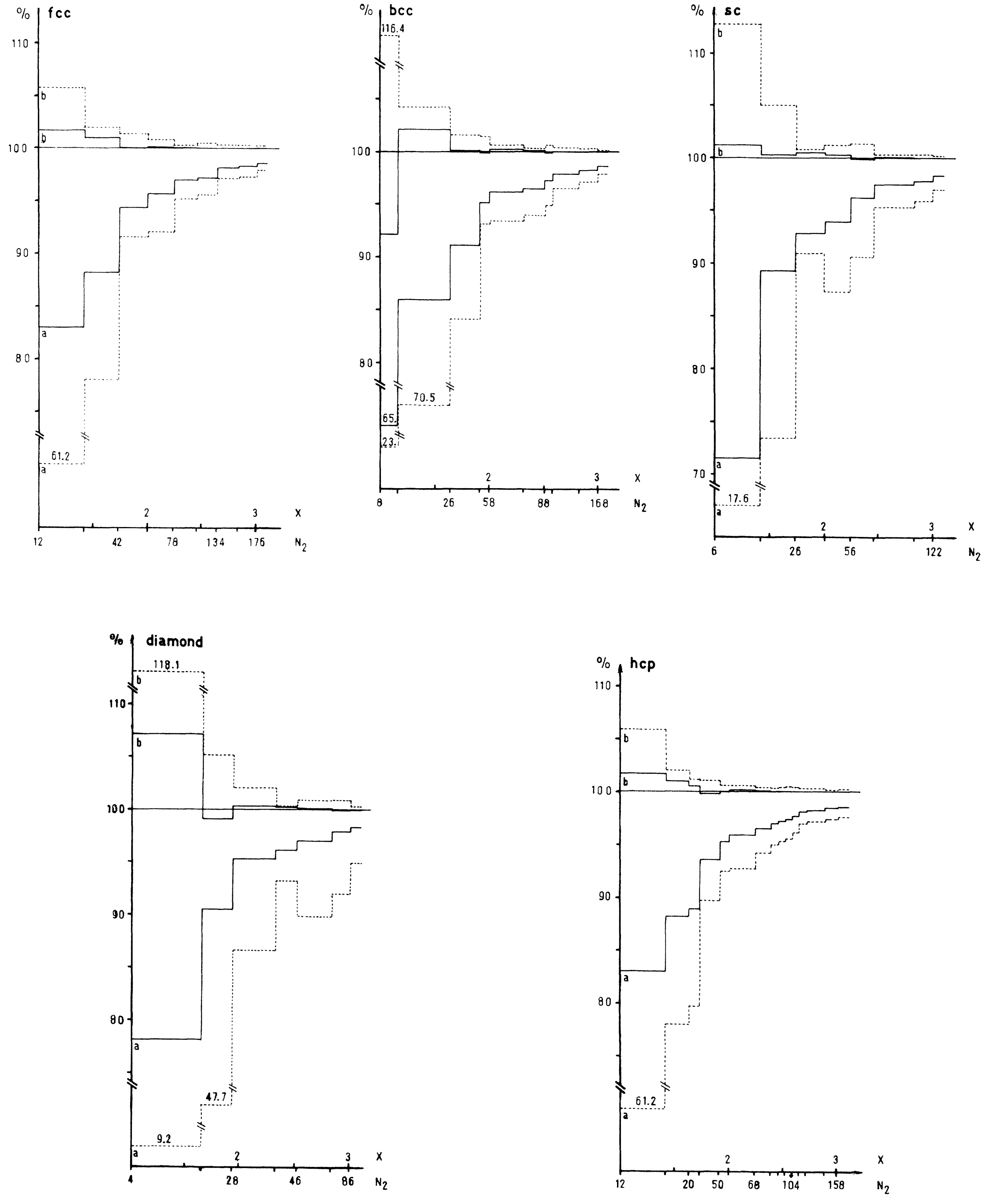

FIG. 3. Convergence of $G_2(R_i)$, G_2, $G_3^*(R_i)$, and G_3 to their limiting values, as a function of x and N_2 (see text). Solid lines: two-body interactions. Dotted-lines: three-body interactions. (a) $G_2(R_i)$, $G_3^*(R_i)$; (b) G_2, G_3.

sake of completeness, we have also included hcp, taking the limiting values $G_2(\infty)=10.841\,167$ (Ref. 17) and $G_3(\infty)=7.631\,879$ (Ref. 3). It can be seen that the proposed approximation works extremely well: The error in the extrapolated values of G_2 and G_3 is less than 1% already for $N_2 \lesssim 50$, $N_3 \lesssim 1000$ ($x \lesssim 2$).

TABLE I. "Limiting values" of the geometrical factors G_2 and G_3 for lattices with isotropic bodies. In all cases, R_i has been chosen to include atoms up to $5R_0$, the corresponding nearest-neighbor distance, and the unit length is defined as $d_0=R_0/\sqrt{2}$. Also included are the number of pairs and triplets, N_2 and N_3, and of symmetry independent pairs and triplets, $\mathcal{N}_2$ and $\mathcal{N}_3$, and the partial contributions to G_2 and G_3.

	fcc $R_i=7.1545$	bcc $R_i=7.1425$	sc $R_i=7.0321$	Diamond $R_i=7.1864$
N_2	766	700	5.14	356
$\mathcal{N}_2$	31	33	26	28
$G_2(R_i)$	10.806 046	9.158 498	6.275 868	3.822 070
$\Delta G_2(R_i)$	0.034 314	0.031 678	0.025 552	0.015 551
G_2	10.840 360	9.190 176	6.301 421	3.837 621
N_3	292 995	244 650	131 841	63 190
$\mathcal{N}_3$	6649	5811	3244	2935
$G_{TTT}(R_i)$	7.604 568	5.857 522	2.618 794	0.657 838
$G_{TFT}(R_i)$	−0.013 464	−0.011 611	−0.006 994	−0.002 884
$G_3(R_i)$	7.564 175	5.822 689	2.597 811	0.649 185
$\Delta G_3(R_i)$	0.069 749	0.058 950	0.036 234	0.014 197
G_3	7.633 928	5.881 639	2.634 045	0.663 383
G_3[a]	7.630±0.003	5.875±0.008	2.632±0.001	

[a] High precision values from Ref. 4.

B. Bodies with cylindrical symmetry: *Pa*3 and *Cmca* structures

In order to study the effect of anisotropy on the three-body interactions, we have taken as examples the two structures *Cmca* and *Pa*3. Many crystals of small linear molecules crystalize in these structures (N_2, halogens, acetylene) for which different types of two-body interactions have been extensively studied.[18]

The direct sums $G_2(R_i)$ and $G_3(R_i)$ have been performed using the general expressions, Eqs. (5) and (6); the extrapolations were made using the spherical approximations [Eqs. (13) and (18)–(20)]. *Pa*3 has an underlying fcc structure; the molecules are aligned along the cube diagonals. We have used an idealized form of *Cmca* with $a=b=c$, which has the same underlying point lattice as *Pa*3. In this case, the molecules are stacked in layers parallel to the *bc* plane. Several sets of calculations for different molecular orientations, $\hat{\mathbf{z}}$, have been performed. The orientation is defined by the two polar angles, such that

$$\cos\theta=\hat{\mathbf{z}}\cdot\hat{\mathbf{a}}\ ,\quad \tan\phi=\hat{\mathbf{z}}\cdot\hat{\mathbf{c}}/\hat{\mathbf{z}}\cdot\hat{\mathbf{b}}\ .$$

In this way $\cos\theta=0$ corresponds to the *Cmca* structure, and $\cos\theta=1/\sqrt{3}$, $\tan\phi=1$ to the *Pa*3 structure. A value of $x=2$ ($N_2=54$) was used in all cases. In order to esti-

TABLE II. Lattices parameters, polarizabilities, geometrical factors, and ratios of two- and three-body dispersive energies of chlorine, α- and β-acetylene, and nitrogen.

	Cl_2	Acetylene β (*Cmca*)	 α (*Pa*3)	N_2
a (Å)	6.207[a]	6.188[b]	6.091[c]	5.644[d]
b (Å)	4.441	6.002		
c (Å)	8.117	5.547		
α (Å^3)[e]	4.606	3.490		1.767
K	0.188	0.177		0.131
G_2 (Å^{-6})	0.014 811	0.016 099	0.013 267	0.021 187
G_3 (Å^{-9})	0.000 358	0.000 433	0.000 321	0.000 652
$\lvert W_3^{(1)}/W_2^{(1)}\rvert$	0.1114	0.0938	0.0845	0.0544

[a] Reference 23.
[b] Reference 24.
[c] Reference 25.
[d] Reference 26.
[e] Reference 19.

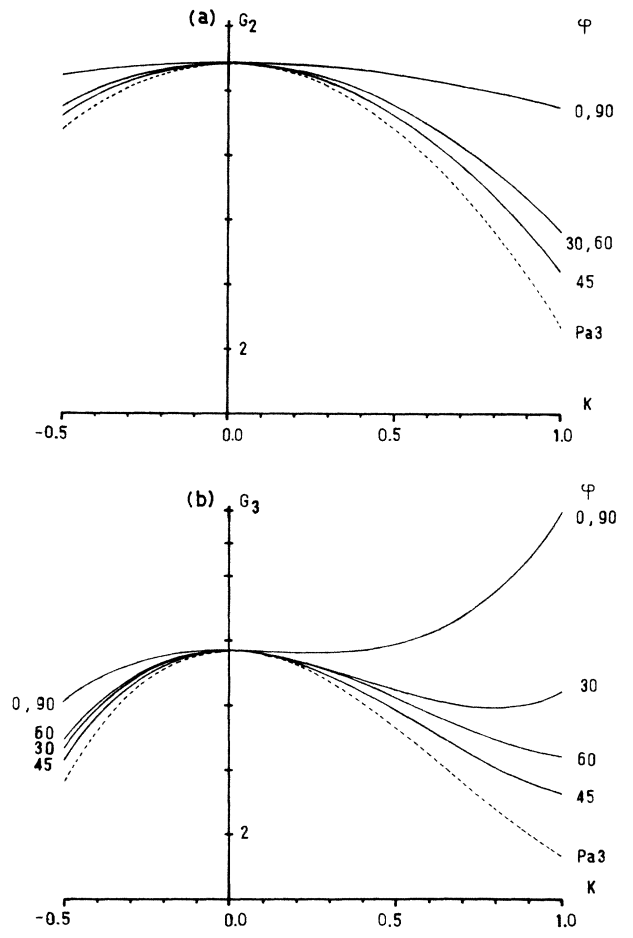

FIG. 4. Geometrical factors for the *Pa*3 and *Cmca* structures, as a function of the polarizability anisotropy *K*, for different molecular orientations in *bc* plane. (a) G_2; (b) G_3.

mate the accuracy of the approximation, in one particular case ($\theta=0$) of very high molecular anisotropy ($K=0.5$) we extended the direct sum to $N_2=380$. The differences between the two cases were $\sim 0.33\%$ in G_2 and $\sim 1.9\%$ in G_3.

Figure 4 shows the results of the calculation for several values of ϕ in the *Cmca* structure, and for the *Pa*3 structure, as a function of the polarizability anisotropy *K*, between its extreme values $-0.5<K<1$. Calculations for $\phi=\pi/4$ and θ varying between 0 and $\pi/2$ lie between the extreme curves in Fig. 4. From Eqs. (5)–(7) it is clear that G_2 and G_3 are quadratic and cubic functions, respectively, of the anisotropy *K*. For our calculations, this dependence results as

$$\left.\begin{aligned} G_2&=10.848-8.103K^2\\ G_3&=7.684-12.930K^2+6.533K^3 \end{aligned}\right\} \text{ for } Pa3\ , \tag{21a}$$

$$\left.\begin{aligned} G_2&=10.848-6.409K^2\\ G_3&=7.684-10.371K^2+5.906K^3 \end{aligned}\right\} \text{ for } Cmca,\ \phi=\pi/4\ . \tag{21b}$$

Our results for the *Pa*3 structure, which were obtained for $x=2$ ($N_3=1431$) are less than 1% higher than those reported by Monson and Rigby,[9] who used $x=5$ ($N_3=292\,995$) and corrected their results by supposing that for $x>5$ the summation could be approximated using the contribution found in the isotropic case. If we change the isotropic term in Eq. (21a) from 7.684 to the high precision value 7.63, both results differ by less than 0.3%.

It is important to note that both G_2 and G_3 are positive for all structures and possible values of *K*, and therefore always $W_2<0$ and $W_3>0$. For most real molecules *K* ranges between $-\frac{1}{4}$ and $\frac{1}{4}$,[19] and in this interval both G_2 and G_3 are little dependent on the value of *K* and on the molecular orientation.

C. Crystals of acetylene, chlorine, and nitrogen

We have calculated the two- and three-body dispersive energies of the crystals of Cl_2 (*Cmca*), α-nitrogen (*Pa*3), and both known phases of acetylene (*Pa*3 and *Cmca*). For the geometrical factors of the *Pa*3 structures we have used the results of the preceding section; those for the real *Cmca* structures were calculated using $N_2\simeq 60$. From Eqs. (9) and (4) we get

$$|W_3^{(1)}|/|W_2^{(1)}|=\alpha G_3/G_2\ .$$

Table II shows the corresponding results, and the parameters used in the calculations. It is to be noted that in general $|W_2^{(1)}|>|W_{\text{latt}}|$, the total lattice energy, since the latter includes the short-range repulsive energy; therefore the values of $|W_3^{(1)}/W_2^{(1)}|$ in the table are a lower bound to the contribution of $W_3^{(1)}$ to W_{latt}. For chlorine, for instance, $|W_3^{(1)}/W_2^{(1)}|=11\%$, using $C=38\,000$ kJ/mol,[20] $W_2^{(1)}=-46.9$ kJ/mol; but $W_{\text{latt}}=-32$ kJ/mol, and therefore $W_3^{(1)}$ gives a repulsive contribution of about 16% of W_{latt}.

V. CONCLUSIONS

The extrapolation method presented in this work is extremely efficient and simple. It allows the calculation of G_3, even for anisotropic bodies, with an accuracy of $\sim 2\%$ summing the interactions of as little as $\sim 10^3$ triplets. Although we have dealt with the most important case of dispersive interactions, the model can be easily adapted to other forms of the interaction potential. In addition, for high-symmetry crystals, the symmetry considerations of Sec. III B allow a very large reduction of the amount of computational work. The extrapolation, moreover, may be used with only slight modifications for the calculation of the three-body interactions in disordered solids, liquids, and two-component systems.

The results for the real molecular crystals show some points of interest. The magnitude of the three-body interactions is indeed non-negligible. If, as usual, it is neglected, its effect is somehow included in a reparametrization of the two-body dispersion forces; its magnitude is of the order of entropic contributions to the free energy at room temperature.[21] Even more important, calculations of packing energies of competitive structures in the pairwise approximation often differ by less than 5%.

The relative insensitivity of W_3 to the polarizability anisotropy, and therefore to molecular orientation, indicates that it will probably affect librational motions of the molecules only slightly; but its magnitude suggests that in the case of translational motions, elastic constants, etc, its contribution could be comparable to that of anharmonic effects.[22]

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