PHYSICAL REVIEW B VOLUME 38, NUMBER 18 15 DECEMBER 1988-II

Rapid convergence of lattice sums and structural integrals in ordered and disordered systems

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(Received 22 April 1988)

We present a new interpretation of the Ewald technique that suggests a simple rule to guide the transformation of any lattice sum into a pair of sums, one over the original lattice and the other over the reciprocal lattice, both converging faster than any power law in the distance from the origin. The rule sets conditions needed in finding an approximation to the long-range part of the function being summed, and it is the Fourier transform of this approximation that then appears in the reciprocal-lattice sum. Once such an approximation is found, the same transformation can be used not only for lattice sums over Bravais lattices or lattices with a basis, but also for the structural integrals associated with noncrystalline systems, including glasses and liquids. The approach can also be applied to quasicrystals, where the transformation takes two different forms depending on whether the sum is viewed in three dimensions or six, for the icosahedral case. Finally, other implications of the interpretation are presented, including a set of conditions under which an alternative planewise summation method can be used.

I. INTRODUCTION

A general problem in calculating cohesive energies,[1-5] in the dynamical theory of crystals,[6] in calculating defect energies,[7] and in the use of pseudopotentials,[8] is the evaluation of the sum of terms originating with a function evaluated at the points of a crystal lattice. This function might for instance be based on the interionic pair potential for some system, and may include oscillating phase factors. Since pair and higher-center potentials are often of long range, the corresponding lattice sums are only very slowly convergent or, as is the case for the Coulomb potential, may only be conditionally convergent. This means that direct evaluation of the sums even by computer is impractical if high accuracy is required, and in consequence an initial rearrangement or transformation is needed to improve the convergence.

Many techniques have been used in the past to achieve such a rearrangement. The most useful for the simple Coulomb problem on a three-dimensional lattice was first proposed by Ewald,[9,10] and was soon thereafter extended to arbitrary power laws by Misra[2] and by Born and Bradburn;[11] it has since been developed further in various ways.[3,4,8,12-14] All these Ewald-like methods split the potential into two pieces, one a sum over the original lattice and the other transformed by the Poisson relation to a sum over the reciprocal lattice. For a function in a given number of dimensions, the same transformation can be used with any Bravais lattice. Other methods, in contrast, generally require specification of the lattice before the transformation is made. A second commonly used approach, also quite general, is the planewise summation technique.[15-17] Instead of splitting the sum into two pieces, this method separates the fundamental lattice translation vectors into two subsets and the Poisson formula is applied to the sum over the lattice generated by just one of them. The final sum is then over a lattice which in some directions is the real-space lattice, and in others is the reciprocal lattice. There are other possible rearrangements to produce rapidly converging series, such as the Schlömilch series of Hautot.[18] These are usually restricted to a small class of sums, but they may produce even faster convergence than the Ewald-like methods since the entire sum is expressed as an analytic function which is then approximated by a rapidly converging series. For the Ewald-like methods the final expression still contains sums over the lattice sites, or possibly integrals over the correlation functions for a noncrystalline material.

In this paper we first point out a very simple explanation of the success of the Ewald and similar methods, by appealing to a widely known property of the convergence of Fourier series for a smooth function. In hindsight it seems surprising that this observation has not been made before; possibly it has been obscured by previous derivations and their notations, since it becomes very clear once the problem is cast in a general form. In any case, this new understanding of the Ewald method allows us to generalize it even further, and to apply it immediately to almost any lattice sum. The same result also gives an understanding of when the planewise methods can work, which we examine in Sec. IV.

The present paper was stimulated by the need to evaluate lattice sums for an icosahedral quasicrystal.[19] This is in fact a three-dimensional structure, but is most easily derived from a periodic six-dimensional structure, leading to a problem involving six-dimensional lattice sums. As mentioned above, an advantage of the Ewald approach is that it does not depend on the structure of the underlying lattice, so that it can even be applied to noncrystalline materials if the structure in real and reciprocal space is precisely known. Applying it directly to the quasicrystal transforms the "true" (||) space parts into rapidly converging functions, but the six-dimensional sum also extends into the "complementary" ($\perp$) space where in reciprocal space the new "potential" decays only as $k_\perp^{-4}$ or even more slowly in those three dimensions. This means that the sum is still only power-law convergent in these particular directions, and points to a need for generalizing the Ewald formula.

A slightly different application of the convergence techniques to be discussed below is in evaluation of the numerical Fourier transform of certain functions. In this problem it is advantageous to analytically transform any singular parts and any long-range parts separately to obtain an expression that is then easily integrated numerically, with a transform that itself decays in a reasonable manner.

II. LATTICE SUMS—GENERAL DISCUSSION

The problem at hand is to evaluate

$$E[f]=\frac{1}{N}\left\langle\sum_{i,j} f(\mathbf{R}_i-\mathbf{R}_j)\right\rangle , \tag{1}$$

where i (and j) label the points $\mathbf{R}_i$ of a d-dimensional structure, nominally representing the positions of ions in a solid, and with f some interaction potential. The average implied by $\langle\ \rangle$ is quite arbitrary and has no effect on the calculations to follow; it may therefore be evaluated in whatever manner is physically appropriate to the system under consideration. In general, the points $\mathbf{R}_l$ do not have to lie on a simple lattice. They may be points of a lattice with a basis, the coordinates of a noncrystalline solid, or a single configuration of a liquid. In general the lattice sum becomes a structural integral, depending on the pair density

$$\rho^{(2)}(\mathbf{r}-\mathbf{r}')=\left\langle\sum_{i\neq j}\delta(\mathbf{r}-\mathbf{R}_i)\delta(\mathbf{r}'-\mathbf{R}_j)\right\rangle . \tag{2}$$

Note that the system under consideration may be either finite or infinite. For infinite structures we first assume a finite number N of ions in a volume V and then take the limit $N\to\infty$ (with $v_0=V/N$ fixed). Inserting

$$1=\int d^d\mathbf{r}\,\delta(\mathbf{r}-\mathbf{R}_i)\int d^d\mathbf{r}'\delta(\mathbf{r}'-\mathbf{R}_j)$$

in the statistical average in (1) gives us

$$\begin{aligned}E[f]&=f(\mathbf{0})+\frac{1}{N}\int d^d\mathbf{r}\int d^d\mathbf{r}'f(\mathbf{r}-\mathbf{r}')\rho^{(2)}(\mathbf{r},\mathbf{r}')\\&=\int d^d\mathbf{r}\,f(\mathbf{r})P(\mathbf{r}) ,\end{aligned} \tag{3}$$

where

$$\begin{aligned}P(\mathbf{r})&=\frac{1}{N}\sum_{i,j}\delta(\mathbf{r}-(\mathbf{R}_i-\mathbf{R}_j))\\&=\delta(\mathbf{r})+\frac{1}{N}\int d^d\mathbf{r}'\rho^{(2)}(\mathbf{r}',\mathbf{r}+\mathbf{r}') .\end{aligned} \tag{4}$$

Note that we have included the term $i=j$ in the sum (1). This was done to make the Fourier transform of P as simple as possible in the crystal case. However, in practice it is generally necessary to subtract both this self-interaction term and also the energy term associated with a uniform distribution of ions, which means replacing P by

$$P'(\mathbf{r})=P(\mathbf{r})-\delta(\mathbf{r})-\frac{1}{v_0} . \tag{5}$$

In what follows, we do not assume this, but it is a simple matter to include these subtractions if necessary. In the example of the Coulomb interaction, the last term has the effect of including the effect of a uniform negative compensating background. There are subtleties arising from the conditional nature of the convergence here, arising for example from the fact that the average electrostatic potential in an infinite crystal is not well defined.[20] However, the use of (5) is the standard technique for dealing with such background subtractions and yields the physically correct results in most situations.[21]

In a Bravais lattice, we then have $P(\mathbf{r})=\sum_l\delta(\mathbf{r}-\mathbf{R}_l)$ for lattice translation vectors $\mathbf{R}_l$, and in general $P(\mathbf{r})$ is the ion-pair correlation function.

The crucial step common to all the Ewald-like procedures is to divide the sum into a real-space piece and a reciprocal-space piece, where the second term is obtained through the Poisson transformation.[22] More specifically, writing

$$f(\mathbf{r})=\int\frac{d^d\mathbf{k}}{(2\pi)^d}\tilde{f}(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}} , \tag{6}$$

we can immediately obtain the Poisson transform for the lattice sum (1):

$$\begin{aligned}E[f]&=\int\frac{d^d\mathbf{k}}{(2\pi)^d}\tilde{f}(\mathbf{k})\cdot\int d^d\mathbf{r}\,e^{i\mathbf{k}\cdot\mathbf{r}}P(\mathbf{r})\\&=\int\frac{d^d\mathbf{k}}{(2\pi)^d}\tilde{f}(\mathbf{k})\tilde{P}(-\mathbf{k}) .\end{aligned} \tag{7}$$

For a crystal lattice we find

$$\tilde{P}(-\mathbf{k})=\sum_l e^{i\mathbf{k}\cdot\mathbf{R}_l}=N\sum_l\delta_{\mathbf{k},\mathbf{K}_l} , \tag{8}$$

where the $\mathbf{K}_l$ are the points of the corresponding reciprocal lattice, and since in a volume V the volume per distinct $\mathbf{k}$ in reciprocal space is $(2\pi)^d/V$, then

$$\tilde{P}(-\mathbf{k})=\frac{(2\pi)^dN}{V}\sum_l\delta(\mathbf{k}-\mathbf{K}_l) , \tag{9}$$

so

$$E[f]=\sum_l f(\mathbf{R}_l)=\frac{1}{v_0}\sum_l\tilde{f}(\mathbf{K}_l) , \tag{10}$$

where v_0 is the volume per ion. In a liquid or glass, this $\tilde{P}(\mathbf{k})$ is exactly v_0 times the static structure factor $S(\mathbf{k})$, except that it also includes a δ function at $\mathbf{k}=\mathbf{0}$ [which is removed if the subtractions (5) are applied]. However, the crystal-lattice result (10) is the standard form for the Poisson transformation.

The Ewald technique in its most general form can now be stated succinctly. Given $f(\mathbf{r})$, we are required to find a function $g(\mathbf{r})$ such that $h(\mathbf{r})=f(\mathbf{r})-g(\mathbf{r})$ decays rapidly in real space, and such that Fourier transform $\tilde{g}(\mathbf{k})$ decays rapidly in reciprocal space. Assuming these conditions have been met, and taking for the moment only the crystalline case, then

$$E[f]=\sum_l h(\mathbf{R}_l)+\sum_l g(\mathbf{R}_l)$$
$$=\sum_l h(\mathbf{R}_l)+\frac{1}{v_0}\sum_l \tilde{g}(\mathbf{K}_l)\ , \tag{11}$$

where the Poisson relation has been applied only to the second term here. The result is a pair of sums, one in real space and the other in reciprocal space, and both are rapidly converging provided an appropriate function $g(\mathbf{r})$ is found. The approach of Sugiyama[7] suggests that the search can be carried out systematically, but is not itself complete since, for example, it fails when the initial function f has a singular line or plane.

A good example of the Ewald approach is the general method of Misra,[2] and of Born and Bradburn,[11] who proceeded from Ewald's result for the Coulomb potential to produce functions which allow evaluation for any power law or product of a polynomial in the position coordinates with an inverse power law. We give here their results expressed in most general form. With the $1/r^m$ potential function we can use incomplete Γ functions, which for integer values of m reduce to Gaussians or to error functions; thus,

$$f(r)-g(r)=h(r)=\frac{1}{r^m\Gamma(m/2)}\Gamma\left[\frac{m}{2},v^2r^2\right]\ , \tag{12}$$

with the reciprocal-space part

$$\tilde{g}(k)=\frac{\pi^{3/2}}{\Gamma(m/2)}\left[\frac{2}{k}\right]^{3-m}\Gamma\left[\frac{3-m}{2},\frac{k^2}{4v^2}\right]\ . \tag{13}$$

This immediately reproduces the original Ewald result for $m=1$ or 2. Thus, for $f(\mathbf{r})=e^{i\alpha\cdot\mathbf{r}}/r^m$ (the exponential shifts the origin of reciprocal space by α) we find

$$E[f]=\sum_l \frac{e^{i\alpha\cdot\mathbf{R}_l}}{R_l^m}\frac{1}{\Gamma(m/2)}\Gamma\left[\frac{m}{2},v^2R_l^2\right]$$
$$+\sum_l \frac{\pi^{3/2}}{\Gamma(m/2)}\left[\frac{2}{|\mathbf{K}_l-\alpha|}\right]^{3-m}$$
$$\times\Gamma\left[\frac{3-m}{2},\frac{(\mathbf{K}_l-\alpha)^2}{4v^2}\right]\ , \tag{14}$$

and multiplying the potential by a polynomial we then have

$$E\left[\frac{Q(\mathbf{r})e^{i\alpha\cdot\mathbf{r}}}{r^m}\right]=Q\left[\frac{1}{i}\frac{\partial}{\partial\alpha}\right]E\left[\frac{e^{i\alpha\cdot\mathbf{r}}}{r^m}\right]\ , \tag{15}$$

where Q is any polynomial. Kornfeld[23] used a similar strategy to derive results for the multipole potentials starting from the Coulomb result.

These functions [(12) and (13)] are extremely useful for calculations of lattice dynamics[6] and have also been extended, for example, to treat lattices with a basis[12] or even to potentials with Friedel oscillations.[3,4,7] The great advantage here is that the method can be applied to a wide variety of functions on any kind of lattice. However, there is a price, namely that a *pair* of lattice sums still remains in the final expression, so that the other lattice-specific methods might in some cases be more efficient.

III. RESTRICTIONS ON THE CHOICE OF FUNCTIONS g

The main step in understanding the success of the method for certain functions g is the following lemma, which is itself based on a relatively well-known result in approximation theory.[24]

Lemma: If (i) $f(\mathbf{r})$ is a C^∞ function, and (ii) there exists some N for which all nth derivatives of f are absolutely integrable (for all $n>N$), then $\tilde{f}(\mathbf{k})$ exists and decays at infinity faster than any power law in k.

To prove this, we need only note that for any polynomial Q the Fourier transform of $Q(\partial/\partial\mathbf{r})f(\mathbf{r})$ is $Q(i\mathbf{k})\tilde{f}(\mathbf{k})$. In particular, let us consider $g_n(\mathbf{r})=(\nabla^2)^nf(\mathbf{r})$. Then

$$\tilde{g}_n(\mathbf{k})=\int(\nabla^2)^nf(\mathbf{r})e^{-i\mathbf{k}\cdot\mathbf{r}}d^d\mathbf{r}=(-k^2)^n\tilde{f}(\mathbf{k})\ . \tag{16}$$

However, by the second condition in the lemma we have for all $\mathbf{k}$

$$|\tilde{g}_n(\mathbf{k})|\le\int|(\nabla^2)^nf(\mathbf{r})|d^d\mathbf{r}=C_n\quad\left[n>\frac{N}{2}\right]\ , \tag{17}$$

where C_n is a finite constant. This implies that

$$|\tilde{f}(\mathbf{k})|k^{2n}\le C_n\quad\text{and}\quad|\tilde{f}(\mathbf{k})|\le\frac{C_n}{k^{2n}}\quad\left[n>\frac{N}{2}\right]. \tag{18}$$

Taking the limit $k\rightarrow\infty$ in this last relation implies that $\tilde{f}$ must decay faster than any inverse power of k, as we set out to prove. Note that this also implies that $\tilde{f}$ can have an infinite singularity at $\mathbf{k}=\mathbf{0}$, but nowhere else.

How can this result be applied? Clearly the problem of generalizing the Ewald method is now to find appropriate functions $g(\mathbf{r})$ such that *both* $\tilde{g}$ and $h=f-g$ are rapidly decaying. The lemma therefore asserts that the following rule guarantees a successful division of the lattice sum.

Rule: Given f, choose g (i) to be a "good" approximation to f, (ii) to be a C^∞ function, and (iii) to have all high-order derivatives absolutely integrable.

Here g is a good approximation to f if there exists a set A such that for all $\mathbf{r}$ in A and for any n,

$$|\mathbf{r}|>R\Longrightarrow|f(\mathbf{r})-g(\mathbf{r})|<\frac{C_n}{R^n} \tag{19}$$

and

$$\mu(\{\mathbf{r},\ |\mathbf{r}|>R,\ \mathbf{r}\notin A_R\})<\frac{B_n}{R^n} \tag{20}$$

for all R, where B_n and C_n are finite. Thus, in essence, for large R, g must be exponentially close to f, except possibly on a set which is itself of exponentially small size.

Now let us consider by way of example the potential $f(r)=1/r^m$ that is dealt with so successfully by the functions (12). We set $g(\mathbf{r})=g_1(r)/r^m$, where we can assume g_1 is spherically symmetric. Our rule requires us to choose g_1 to be smooth except possibly at $r=0$, where the series expansion of g_1 must be of the form

$$g_1(r)=a_0r^m+a_1r^{m+2}+\cdots \ . \tag{21}$$

But we also require, as $r\to\infty$, that $g_1(r)\to 1$ exponentially fast. If we let

$$g_1(r)=\frac{\int_0^r u(r')dr'}{\int_0^\infty u(r')dr'} \ , \tag{22}$$

then the conditions on $u(r)$ are integrability, exponential decay at infinity, and a power-series expansion of the form $u(r)=b_0r^{m-1}+b_1r^{m+1}$ about $r=0$. The simplest choice is then clearly

$$u(r)=r^{m-1}\exp(-\eta r^2) \ ,$$

which is exactly the result (12). We see that the principal reason for the success of (12) is the property of smoothness everywhere. This includes cancellation of the singularity at $r=0$ to leave only even powers of r, since odd powers would produce new square-root singularities at the origin. Finally, as $r\to\infty$ the nth derivatives of g vary as $1/r^{n+m}$, so that for $n>d-m$ we see that these are indeed absolutely integrable. From this we are provided with an automatic guarantee that in *any* dimension $\tilde{g}(\mathbf{k})$ decays faster than any inverse power of k at infinity. In fact, in d dimensions

$$\tilde{g}(\mathbf{k})=\frac{2^{d-m}\pi^{d/2}}{\Gamma(m/2)k^{d-m}}\Gamma\left[\frac{d-m}{2},\frac{k^2}{4\nu^2}\right] \ , \tag{23}$$

which decays to zero roughly as $\exp(-k^2/4\nu^2)$ for any values of d and m.

But the lemma can now easily be applied to *any* function of $\mathbf{r}$, and in particular to the quasicrystal sums mentioned in the Introduction. The result (15) encompasses a large class of functions by replacing the polynomial Q by any function which, when its argument happens to be a derivative, gives an unambiguous differential operator. However, potentials which cannot be obtained in this way require a transformation quite distinct from this class. An excellent example of both this and the application to noncrystalline systems is provided by the Coulomb sum for an icosahedral quasicrystal.

In one model for an icosahedral quasicrystal[25] the locations of metal ions in real space is determined by a projection from a six-dimensional cubic lattice in which the "basis" consists of a three-dimensional ball of radius R_0 in each unit cell. There are then two alternative methods for evaluating this sum. The first is to regard this as a three-dimensional problem, in which $f(r)=1/r$ as for a standard Coulomb sum. Then

$$P(\mathbf{r})=\sum_{\mathbf{R}}\delta(\mathbf{r}-\mathbf{R}_\parallel)P_0\left[\frac{R_\perp}{2R_0}\right] \ , \tag{24}$$

where

$$P_0(x)=[1+(-3x+x^3)/2]\Theta(1-x) \ . \tag{25}$$

The sum in (24) is over the six-dimensional cubic lattice. Then

$$\tilde{P}(\mathbf{k})=\frac{(2\pi)^3}{v_0}\sum_{\mathbf{K}}\delta(\mathbf{k}-\mathbf{K}_\parallel)S_0(2R_0K_\perp) \ , \tag{26}$$

where

$$S_0(x)=[3(\sin x-x\cos x)/x^3]^2 \ , \tag{27}$$

v_0 is the volume per ion in this structure, and the reciprocal vectors $\mathbf{K}$ run over the six-dimensional reciprocal lattice.

We then apply (7) to this noncrystalline problem, using the standard three-dimensional Ewald formula, to obtain

$$\begin{aligned}E=&\sum_{\mathbf{R}\neq 0}\frac{\operatorname{erfc}(\eta R_\parallel)}{R_\parallel}P_0\left[\frac{R_\perp}{2R_0}\right]-\frac{\pi}{\eta v_0}\\&+\frac{1}{v_0}\sum_{\mathbf{K}\neq 0}\frac{4\pi\exp(-K_\parallel^2/4\eta)}{K_\parallel^2}S_0(2R_0K_\perp)\\&-2(\eta/\pi)^{1/2} \ .\end{aligned} \tag{28}$$

We have included the subtractions referred to in (5) to demonstrate that they are indeed easy to apply. Both sums are absolutely convergent, since in the perpendicular directions the first is cut off at $R_\perp=2R_0$ and the second falls as $1/K_\perp^4$. We have found (28) to be useful in obtaining rough values for the Madelung energy.

However, the summations above *are* over a six-dimensional lattice, even though the real structure is three dimensional, and in particular the reciprocal-space sum does not converge rapidly in the perpendicular directions. There is an alternative method, however, which is to consider the original problem as a sum of the six-dimensional function $f(\mathbf{r})=P_0(\mathbf{r}_\perp/2R_0)r_\parallel$, over a six-dimensional cubic lattice. The problem thus becomes one of finding a smooth approximation to this that satisfies our rule in six dimensions. The function $P_0(r_\perp/2R_0)\operatorname{erf}(\eta r_\parallel)/r_\parallel$ used in (28) does not, since although it removes the singularity at $r_\parallel=0$, others remain at $r_\perp=2R_0$ and $r_\perp=0$, and, furthermore, since there are points with $r_\parallel$ close to zero with $r_\perp$ arbitrarily large, our condition (i) is also not satisfied. It is these singularities that are responsible for the $1/K_\perp^4$ behavior seen above.

There are, in fact, many functions g that completely satisfy our rule. One of the simplest is

$$g(\mathbf{r})=\tfrac{1}{2}\{1+\operatorname{erf}[a(4R_0^2-r_\perp^2)e^{\eta r^2}]\}\frac{\operatorname{erf}(br_\parallel e^{\eta r^2})}{r_\parallel}\left\{1+\left[-\frac{3}{2}\frac{r_\perp}{2R_0}+\frac{1}{2}\left[\frac{r_\perp}{2R_0}\right]^3\right]\operatorname{erf}(cr_\perp e^{\eta r^2})\right\} \ . \tag{29}$$

This is smooth, since it has the correct properties at $r_\perp=0$, $r_\parallel=0$, and $r_\perp=2R_0$, and thus satisfies our condition (ii). The magnitude of its derivatives is exactly as for $f(\mathbf{r})$ itself for large r, and the smoothness for small r implies that condition (iii) is also necessarily satisfied. Finally, the presence of the factors of $\exp(\eta r^2)$ allow this to satisfy our first condition. If these were absent, the real-space sum would not converge well, as the singular region $r_{\parallel}=0$ extends to $r_{\perp}=\infty$ with a width that decreases at most as a power law. This factor ensures that the size of the singular region decreases exponentially at large r.

Of course, the Fourier transform $\tilde{g}(\mathbf{k})$ must be determined numerically, which adds to the computational time. However, the error remaining with the first method decreases roughly as the inverse one-sixth power of the computational time, whereas for the second the error remaining would be exponentially decreasing in time, except for the numerical integral. The integration again results in a power-law decay with computation time, but with a power law of roughly -4, which is a considerable improvement. However, the overhead involved with the second method in this specific problem[19] means that it becomes faster only at an accuracy of about 10^{-4}.

It is a simple matter to extend these techniques to a lattice with a basis, a finite-sized lattice, or the liquid and glass systems by applying Eq. (3) in the real-space part, and Eq. (7) in the reciprocal space, using the appropriate pair correlation function $P(\mathbf{r})$. The first method in the quasicrystal case discussed above is an example of how to do this in general, and it should be clear that these transformations are practical in many different systems.

As a final note, consider the numerical computation of the Fourier transform of any function $f(\mathbf{r})$. If f is known at large $\mathbf{r}$, perhaps in terms of some expansion in inverse powers of r, then by subtracting smooth functions, such as the g's above, with analytically known Fourier transforms, we can successively eliminate higher and higher powers of $1/r$, making the final necessary real-space integral considerably easier to evaluate. If f also has known singularities at certain finite $\mathbf{r}$, these may be removed by subtracting functions such as the h's. If both of these subtractions can be accomplished, then the final function in the numerical integral is everywhere finite and also decays more rapidly at infinity. The resulting computations are then very much easier.

IV. PLANEWISE METHODS REVISITED

The rule for the Ewald-like methods above has an analog for the planewise methods that we now discuss. As mentioned in the Introduction, the key step in planewise summation is to split the lattice Λ into two sublattices Λ_1 and Λ_2, which is accomplished by dividing the fundamental lattice vectors into two sets, and generating the sublattices from these sets. If we wish to treat noncrystalline materials (so far as we are aware no such application has previously been made) this means splitting the vector space R^d into two subspaces S_1 and S_2; in the crystalline case these become the vector spaces spanned by the two lattices. In any case, writing the points of R^d as $\mathbf{r}=(\mathbf{r}_1,\mathbf{r}_2)$ and writing the points $\mathbf{k}$ of reciprocal space similarly, we obtain

$$f(\mathbf{r})=\int_{\tilde{S}_2}\frac{d^{d_2}k_2}{(2\pi)^{d_2}}\hat{f}(\mathbf{r}_1,\mathbf{k}_2)e^{i\mathbf{k}_2\cdot\mathbf{r}_2} \tag{30}$$

and thus

$$\begin{aligned}E[f]&=\int\frac{d^{d_2}k_2}{(2\pi)^{d_2}}\int d^{d_1}r_1\hat{f}(\mathbf{r}_1,\mathbf{k}_2)\\&\qquad\times\int d^{d_2}r_2e^{i\mathbf{k}_2\cdot\mathbf{r}_2}P(\mathbf{r}_1,\mathbf{r}_2)\\&=\int\frac{d^{d_2}k_2}{(2\pi)^{d_2}}\int d^{d}r_1\hat{f}(\mathbf{r}_1,\mathbf{k}_2)\hat{P}(\mathbf{r}_1,-\mathbf{k}_2)\ .\end{aligned} \tag{31}$$

For a crystal lattice, the pair distribution function is

$$P(\mathbf{r})=\sum_{l_1}\sum_{l_2}\delta(\mathbf{r}_1-\mathbf{R}_{l_1})\delta(\mathbf{r}_2-\mathbf{R}_{l_2})\ , \tag{32}$$

which leads to the intermediate function

$$\begin{aligned}\hat{P}(\mathbf{r}_1,-\mathbf{k}_2)&=N_2\sum_{l_1,l_2}\delta(\mathbf{r}_1-\mathbf{R}_{l_2})\delta_{\mathbf{k}_2,\mathbf{K}_{l_2}}\\&=\frac{(2\pi)^{d_2}}{v_{02}}\sum_{l_1,l_2}\delta(\mathbf{r}_1-\mathbf{R}_{l_1})\delta(\mathbf{k}_2-\mathbf{K}_{l_2})\ .\end{aligned} \tag{33}$$

The lattice sum may therefore be written simply as

$$E[f]=\frac{1}{v_{02}}\sum_{l_1}\sum_{l_2}\hat{f}(\mathbf{R}_{l_1},\mathbf{K}_{l_2})\ , \tag{34}$$

which is a single sum over this new "half-transformed" lattice, with v_{02} the volume per unit cell in the sublattice Λ_2.

Therefore, for this method to succeed, we must have rapid convergence of $\hat{f}$ in both the real- and reciprocal-space parts. In turn, the conditions for this to occur are now clear from the lemma of the preceding section. Assuming integrability of the terms, the requirements are (1) $f(\mathbf{r}_1,\mathbf{r}_2)$ must be smooth, considered as a function of $\mathbf{r}_2$ alone, *and* (2) $\tilde{f}(\mathbf{k}_1,\mathbf{k}_2)$ must be smooth, considered as a function of $\mathbf{k}_1$ alone.

As an example of this method we can again consider the $1/r^m$ potential. Although this planewise method is quite general, the general expressions simplify in the special case of a cubic lattice. Therefore, for convenience we will assume here that we wish to evaluate this over a three-dimensional simple-cubic lattice. Labeling the cubic indices i,j,l gives

$$E=\sum_{i,j,l}\frac{1}{(i^2+j^2+l^2)^{(m/2)}}\ . \tag{35}$$

Let $\mathbf{r}_1=[i,j]$, and $\mathbf{r}_2=[l]$. Clearly, $f(\mathbf{r}_1,\mathbf{r}_2)$ is smooth as a function of $\mathbf{r}_2$ alone so long as $[i,j]\neq 0$. Since $\tilde{f}$ is

$$\tilde{f}(\mathbf{k})=4\pi\frac{\Gamma(2-m)}{k^{3-m}}\sin(m\pi/2)\ ,$$

this is also smooth as a function of $\mathbf{k}_1$ alone, provided again that $\mathbf{k}_2\neq 0$. Thus we are guaranteed that the planewise method will work in this case. Indeed, for the simple case $m=2$ we obtain a function

$$\hat{f}(\mathbf{r}_1,\mathbf{k}_2)=\frac{\pi}{r_1}\exp(-r_1k_2)\ , \tag{36}$$

where $r_1=(i^2+j^2)^{1/2}$ and $k_2=2\pi|k'|$ for k' an index of the reciprocal-lattice sum. The cases $i=j=0$ and $k'=0$

must be evaluated separately, but these reduce to lower-dimensional sums, and can therefore be treated similarly.

For applications and a more detailed treatment of this planewise approach, see the references below, particularly the paper by Sholl.[15-17]

V. CONCLUSIONS

From our results here it should be apparent that almost any lattice sum involving a long-range potential can be split into real-space and reciprocal-space pieces that are rapidly converging. The previous generalizations of Ewald's method already cover a wide class of functions, which has since been expanded by a variety of extensions. The lemma of Sec. III now explains the underlying principle of these techniques, and in addition demonstrates that similar results may be easily obtained for other types of long-range potentials. The lemma shows why the planewise methods are also quite successful for some potentials, but they appear to have a somewhat smaller range of application. An illustration of the usefulness of this result, aside from explaining how to do $(1/r^m)$-type potentials, is in the calculation of the Madelung energy and similar structure integrals for a quasicrystal. It is clear that the techniques may be applied equally to similar calculations in liquids and glasses. We have also indicated the possibility of application to numerical Fourier transforms, which in essence follows the general rule for division of functions into short-ranged and very smooth long-ranged pieces. The approach therefore has a potential applicability well outside the immediate domain of lattice sums.

ACKNOWLEDGMENTS

We would like to thank Zachary Levine and Chris Rapcewicz for discussions on various aspects of our work. This work has been supported by the National Science Foundation under Grant No. DMR-87-15590, and one of us (A.P.S.) would also like to acknowledge support from the National Sciences and Engineering Research Council (Canada).

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