PHYSICAL REVIEW B VOLUME 19, NUMBER 8 15 APRIL 1979

Scattering from a corrugated hard wall: Comparison of boundary conditions

G. Armand and J. R. Manson*

Centre d'Etudes Nucléaires de Saclay, Service de Physique Atomique, Section d'Etudes des Interactions Gaz-Solides, Boîte Postale 2, 91190 Gif-sur-Yvette, France

(Received 14 July 1978)

The calculation of the scattered-wave amplitude by a hard-corrugated-wall potential is reduced to the determination of a source function, which is then calculated by application of an appropriate boundary condition. We discuss and compare the general features of the solution given by three different boundary conditions: (i) setting the wave function equal to zero on the corrugated surface, (ii) setting the wave function equal to zero on a plane beneath the surface, and (iii) the Rayleigh condition. It is argued that only the first of these three methods will always produce a solution. Detailed comparisons are made for the case of a triangular corrugation profile, and we show that the application of boundary conditions on the surface always gives a solution. However, it is argued that the other two methods cannot produce a convergent solution for this profile, and these conclusions are supported by numerical calculations.

I. INTRODUCTION

The problem of scattering of waves from a hard corrugated wall has been a useful technique for a number of years in the areas of acoustic and electromagnetic waves.[1,2] Recently the problem has been of interest in the field of low-energy atom-surface scattering where the model has been quite successful in interpreting experimental data.[3-6]

The solution of this problem consists in the determination of the so-called "source function" by application of appropriate boundary conditions (physically, the source function is the strength of the wavelets reflected by each part of the hard-wall surface). Since a complete exposition of the theory has been given in detail elsewhere,[4,7,8] we will give here only a brief review and concentrate our attention on the solutions produced by different boundary conditions, that is to say we intend to analyze the different approaches to the problem.

In Secs. II and III we give a review of the three main methods of applying the boundary conditions: (i) the Rayleigh approach, (ii) forcing the wave function to vanish on a plane inside the surface [the Masel-Merrill-Miller (MMM) condition[7]], and (iii) forcing the wave function to vanish on the surface. It is argued that the first two approaches, although very simple to apply, cannot always be made to produce a solution. That is to say, the boundary-condition equations do not always give convergent solutions. However, applying the boundary condition on the surface, in practice a much more difficult procedure, always produces a convergent solution.

In Sec. IV we present calculations for all three methods for the particular example of the triangular surface corrugation in order to substantiate the arguments presented in Sec. II. We are able to demonstrate that, for the method of applying the boundary conditions on the surface, the solution is always convergent. However, a similar analysis gives a strong indication that both the MMM and Rayleigh methods are divergent for the triangular profile and this conclusion is supported by the behavior of the numerical calculations.

II. CORRUGATED-HARD-WALL PROBLEM

In the language of atom-surface scattering the corrugated-hard-wall model is described by a potential which is vanishing outside the surface and infinite inside:

$$V(z,x)=\begin{cases}0, & z>\varphi(x)\\ \infty, & z<\varphi(x)\end{cases}\ , \tag{1}$$

where z is the direction perpendicular to the surface, and $\varphi(x)$ is a periodic function giving the corrugation profile. For simplicity we will consider only the case of a one-dimensional corrugation of period a and total amplitude $2ha$ ($2ha=\varphi_{\max}-\varphi_{\min}$) but the extension to two dimensions is trivial.

The simplest approach to the problem is the one taken by Rayleigh in which one considers the form of the wave function in the asymptotic region $z>\varphi_{\max}(x)$ and assumes that this form can be extended up to the surface. If K_0 and k_{0z} are, respectively, the parallel and perpendicular components of the incident wave vector, the asymptotic form consists of the incident wave plus outgoing diffracted waves:

$$\psi_i=e^{iK_0x}e^{-ik_{0z}z}+\sum_G C_G e^{i(K_0+G)x}e^{ik_{Gz}z}\ , \tag{2}$$

where G is a reciprocal-lattice vector [$G=(2\pi/a)g$,

$g=0,\pm1,\pm2,\ldots]$ and $k_{Gz}^2=K_0^2+k_{0z}^2-(K_0+G)^2$. The boundary condition,

$$\psi=0, \quad z=\varphi(x), \tag{3}$$

is applied directly to (2) giving the defining equation for the coefficients C_G

$$0=1+e^{ik_{0z}\varphi(x)}\sum_G C_G e^{iGx}e^{ik_{Gz}\varphi(x)}. \tag{4}$$

Equation (4) can be Fourier transformed which converts it into an equivalent matrix equation to be inverted for the coefficients C_G

$$B_M=\sum_G C_G Q_{GM}, \tag{5}$$

where

$$B_M=-\delta_{M0} \tag{6a}$$

$$Q_{GM}=\int_0^a dx\, e^{i(G-M)x}\exp[i(k_{Gz}+k_{0z})\varphi(x)]. \tag{6b}$$

Several other methods have been utilized for inverting Eq. (4),[2,5] and in all cases the intensity of the diffracted beams is given by the usual expression

$$I_G=(k_{Gz}/k_{0z})|C_G|^2. \tag{7}$$

The unitarity condition

$$\sum_{G,k_{Gz}\text{ real}} I_G=1 \tag{8}$$

must be satisfied by any calculated result (however, good unitarity by itself is not sufficient to guarantee that the solution is good).

The Rayleigh method is obviously not universally valid because in the region of the potential, $\varphi_{\min}<z<\varphi_{\max}$, the true wave function will, in general, have both incoming and outgoing scattered waves (since each point on the surface acts as spherical emitter of reflected waves).

However, it is not completely correct to call the Rayleigh method an approximation because if by some chance Eq. (4) can be satisfied the result must converge to the true solution, according to the uniqueness theorem obeyed by the wave equation.[9] From a physical point of view one would expect this to happen only when the amplitude of the incoming multiply scattered wave in the selvage region is very small, that is to say, for small h values. Thus we are left with two possibilities, either the Rayleigh method does not converge at all, or it converges to the exact solution. This has been demonstrated to be the case with the sinusoidal corrugation profile in which it is known that the Rayleigh method is correct for small corrugation amplitudes, while for large amplitudes it diverges.[10,11]

The convergence or divergence can be understood in the following way. If Eq. (4) is converted to a matrix equation by some appropriate transformation such as the Fourier transform [Eq. (5)] we have an infinite matrix to invert in order to calculate the scattered amplitude C_G. Obviously in the numerical procedure this matrix is truncated, say to a $N\times N$ matrix. Except for extreme situations such a finite matrix can always be inverted and the C_G calculated values as well as the unitarity sum will depend upon the value of N. For convergent solutions the results will be stable as N is increased to arbitrarily large values, that is to say the I_G approach their asymptotic values and the unitarity sum approaches 1. For a divergent process the results strongly depend upon N and the C_G amplitudes will become unstable with high N values and the unitarity sum will become worse. But in this case, it can happen that for given N values not too large, the result can approximate reasonably the exact solution. This sort of behavior is substantiated by the calculations presented in Secs. III and IV.

Next we present the general formulation of the problem. This can be done with equal facility starting from the Green's-function solution of the Helmholtz equation, or beginning with the integral equations for nonrelativistic scattering theory. Choosing the latter approach the wave function is expressed as

$$\psi_i^{(+)}=\phi_i+\sum_l \phi_l\frac{1}{E_i-E_l+i\epsilon}T_{li}, \tag{9}$$

where ϕ_l is a plane-wave state and T_{li} is the transition matrix

$$T_{li}=\int d\vec{r}\,\phi_l^* V\psi_i^{(+)}. \tag{10}$$

The necessary and sufficient boundary condition at a surface of infinite discontinuity in the potential is that $\psi=0$ on and inside the surface[12]:

$$\psi_i=0;\quad z\leq\varphi(x). \tag{11}$$

The normal derivative of ψ_i is unspecified, and is in fact discontinuous at the surface. Thus Eq. (11) and the condition $V=0$ for $z>\varphi(x)$, together with Schrödinger's equation implies that the product $V\psi_i^{(+)}$ is given by[7]

$$V\psi_i^{(+)}=e^{iK_0x}f(x)\delta(z-\varphi(x)). \tag{12}$$

Equation (12) provides a substantial simplification for the transition matrix appearing in (10) and (9), and after utilizing the periodicity of the surface and carrying out all of the trivial integrals Eq. (9) becomes

$$\psi_i^{(+)} = e^{iK_0 x} e^{-ik_{0z}z} + \sum_G \frac{e^{i(K_0+G)x}}{k_{Gz}} \int_{\text{uc}} dx' F(x') \times e^{-iGx'} \exp[ik_{Gz}|z - \varphi(x')|], \quad (13)$$

where the integral is carried out over the unit cell and

$$F(x) = (-im/\hbar^2 a) f(x).$$

The unknown source function $F(x)$ can be determined by applying the boundary condition

$$\psi_i(z = \varphi(x)) = 0 \quad (14)$$

to ψ_i in Eq. (13).

One is guaranteed an exact solution with this boundary condition because (12) and (14) taken together contain all the information of the necessary and sufficient boundary condition of Eq. (11) and also imply that the potential vanishes for $z > \varphi(x)$. This point has been demonstrated in a previous paper.[8] Thus we have

$$0 = e^{-ik_{0z}b} + \sum_G \frac{e^{iGx}}{k_{Gz}} \int_0^a dx' e^{-iGx'} F(x') \times \exp[ik_{Gz}|b - \varphi(x')|] \quad (15)$$

with $b = \varphi(x)$.

In the asymptotic region $z > \varphi_{\max}$ the wave function (13) consists of an incoming plane wave and outgoing diffracted waves; i.e., the same form as Eq. (2), the starting point for the discussion of the Rayleigh method. The coefficients of the diffracted waves are given by

$$C_G = \frac{1}{k_{Gz}} \int_0^a dx F(x) e^{-iGx} e^{-ik_{Gz}\varphi(x)}. \quad (16)$$

However, in the selvage region $\varphi_{\min} < z < \varphi_{\max}$, it is clear that in general there will be diffracted beams traveling both toward and away from the surface due to the factor $\exp[ik_{Gz}|z - \varphi(x)|]$.

There have been two approaches to the solution of Eq. (15). First the numerical method of Garcia and Cabrera[3] converts the integral equation into a system of linear algebraic equations by a finite difference method. The integral over the unit cell is replaced by a finite sum over $2N$ equally spaced points and the equation is evaluated on an identical grid of $2N'$ points. The resulting system is inverted to obtain $F(x)$ and the coefficients C_G are evaluated by numerical integration of (16). This method, although completely numerical, is very flexible in that it works for a large range of corrugation profiles and has been quite successful in interpreting experimental data.[3,6]

The second approach, taken by the present authors,[8] is to expand $F(x)$ in a complete set of states and invert Eq. (15) by an appropriate transform. In particular if $F(x')$ is expanded in a Fourier series in x'

$$F(x') = \sum_N F_N e^{iNx'} \quad (17)$$

and if Eq. (15) is also Fourier expanded in the variable x we are left with a system of linear equations in F_N which can be expressed in matrix form as

$$0 = A_M(k_{0z}) + \sum_N C_{MN} F_N, \quad (18)$$

where

$$A_M(q) = \int_0^a dx\, e^{-iMx} e^{-iq\varphi(x)}$$

and

$$C_{MN} = \sum_G \frac{1}{k_{Gz}} \int_0^a dx\, e^{i(G-M)x} \int_0^a dx'\, e^{i(N-G)x'} \exp[ik_{Gz}|\varphi(x) - \varphi(x')|] \quad (19)$$

while the coefficients C_G become

$$C_G = \frac{1}{k_{Gz}} \sum_N A_{G-N}(k_{Gz}) F_N. \quad (20)$$

In practice the infinite matrix equation (18) is truncated at a finite dimension and numerically inverted to obtain the F_N

$$0 = F_N + \sum_M C^{-1}_{NM} A_M. \quad (21)$$

The difficulty with this method is the double integral appearing in (19) but for the case of the triangular profile (or any profile consisting of straight-line segments) this integral can be carried out and the calculations are in good agreement with the Garcia-Cabrera method.

A different approach to the problem has been taken in the work of Masel, Miller, and Merrill.[7] Although fully realizing the importance of the boundary condition (14), in order to avoid the mathematical complexities involved with its application they chose a simpler condition, sometimes known as the extinction theorem.[2] The wave function is forced to be identically zero below the surface, i.e., for $z < \varphi_{\min}$. (This procedure is valid subject to the conditions of convergence discussed below.) Putting $\psi_i = 0$ for $z = b = \text{const} = \varphi_{\min}$ in Eq. (15) the same transformation procedure of Eqs. (17)–(21) gives a much simpler equation, which is independent of b, for the same set of coefficients F_N:

$$0 = A'_M + \sum_N C'_{MN} F_N , \tag{22}$$

where

$$A'_M = \delta_{0,M} \tag{23a}$$

and

$$C'_{MN} = \frac{1}{k_{Mz}} A_{M-N}(-k_{Mz}) = \frac{1}{k_{Mz}} \int_0^a dx' \, e^{i(N-M)x'} e^{ik_{Mz}\varphi(x')} . \tag{23b}$$

The matrix C'_{MN} is much simpler than the corresponding matrix C_{MN} of Eq. (19) as it is only a single integral and does not contain the internal summation over reciprocal-lattice vectors.

Masel, Merrill, and Miller have presented calculations using this approach for the sinusoidal surface profile for which the integral in (23b) becomes a Bessel function. The integral can also be carried out for other corrugation profiles including the triangular profile presented in Sec. IV.

This method is clearly simpler than the method of applying the boundary conditions on the surface, however, in practice a number of computational difficulties have been observed. The method seems to converge only for relatively weak surface corrugations.[4]

We would like to point out that this sort of behavior is to be expected. Although the MMM boundary condition is always a necessary condition on ψ_i, it differs substantially from the known necessary and sufficient boundary condition. Consequently there exists the possibility that for some corrugations the MMM condition is not a sufficient condition to produce a solution. Physically, the MMM boundary condition states that the wave function vanishes beneath the surface, but not on the surface itself [except for possibly the denumerably infinite set of points x_n given by $\varphi_{\min} = \varphi(x_N)$]. However, at a surface of infinite discontinuity in V the wave function must vanish both below and on the surface. One can also point out that the MMM condition is redundant in the sense that this information is contained in Eq. (12) which has already been used to solve the general scattering equation [however, Eq. (12) leaves the value of ψ on the surface undetermined]. Of course it can happen, depending on the shape and amplitude of the surface profile, that this condition is sufficient to produce a solution, in which case the solution must be exact and equivalent to the solution given by putting the wave function equal to zero on the surface. This point has been demonstrated by Beeby[14] and follows from the uniqueness theorem. Thus the validity of the method is determined by the criterion of convergence or divergence of the solution as previously pointed out for the Rayleigh case. We also note that, just as with the Rayleigh method, even under divergent conditions a good approximation may be obtained by judicious truncation of the problem.

Calculations supporting precisely this sort of behavior are presented for the triangular profile in Sec. IV. It appears that for this profile both the MMM and Rayleigh methods are divergent, but for small corrugation amplitudes reasonable approximate solutions can be obtained.

III. MATHEMATICAL COMPARISON OF THE THREE METHODS

In this section we would like to present some interesting mathematical comparisons between the three different approaches to the hard-wall problem. First we show how all three approaches are related to a general formalism, and then we show how the Rayleigh and MMM cases can be written as the leading term in an infinite series expansion of the solution using the boundary conditions of Eq. (14).

In all cases, applying the boundary conditions to ψ of Eq. (13) gives

$$0 = e^{-ik_{0z}z} + \sum_G \frac{e^{iGx}}{k_{Gz}} \int_{\text{uc}} dx' \, e^{-iGx'} F(x') \times \exp[ik_{Gz}|z - \varphi(x')|] . \tag{24}$$

Application of the boundary conditions on the surface is effected by setting $z = \varphi(x)$. The MMM conditions are obtained by setting $z = b < \varphi_{\min}$, in which case the absolute magnitude $|z - \varphi(x')|$ becomes $[\varphi(x') - b]$. The Rayleigh method, on the other hand, is obtained by simply removing the absolute magnitude in the exponential of Eq. (24). To see this we replace $|z - \varphi(x')|$ by $[\varphi(x) - \varphi(x')]$, and then note that the resulting integral over the unit cell is exactly the same as for the diffracted beam coefficient of Eq. (16). Thus using Eq. (16) for C_G leads directly to the Rayleigh condition (4).

Now that the connection is established we would like to continue to look at the Rayleigh case in the general formalism with a source function.

In this manner we will obtain a relationship between the Rayleigh approach and the method of applying the boundary condition on the surface.

Replacing $|z - \varphi|$ in (24) by $+[\varphi(x) - \varphi(x')]$ and Fourier transforming the source function as in

(17) we have for the Rayleigh condition

$$0 = e^{-ik_{0z}\varphi(x)} + \sum_G e^{iGx} e^{ik_{Gz}\varphi(x)} \sum_N \frac{F_N}{k_{Gz}} \times \int_{\text{uc}} dx' e^{i(N-G)x'} e^{-ik_{Gz}\varphi(x')} . \tag{25}$$

Fourier transformation of both sides of (25) leaves a matrix relation equivalent to (18) for the Fourier component F_N

$$0 = A_M(k_{0z}) + \sum_N C^{(R)}_{MN} F_N , \tag{26}$$

where

$$C^{(R)}_{MN} = \sum_G \frac{1}{k_{Gz}} \int_{\text{uc}} dx\, e^{i(G-M)x} e^{ik_{Gz}\varphi(x)} \times \int_{\text{uc}} dx'\, e^{i(N-G)x'} e^{-ik_{Gz}\varphi(x')}$$
$$= \sum_G \frac{1}{k_{Gz}} A_{M-G}(-k_{Gz}) A_{G-N}(k_{Gz}) . \tag{27}$$

Equations (26) and (27) are the analogs of Eqs. (18) and (19) for the exact case. Note that $C^{(R)}_{MN}$ is simpler than C_{MN}, being the product of two single integrals rather than a double integral.

To see the relationship between Eq. (18) and Eq. (26) we now write the matrix coefficient (19) in terms of $C^{(R)}_{MN}$

$$C_{MN} = C^{(R)}_{MN} + 2iS_{MN} , \tag{28}$$

where obviously

$$2iS_{MN} = C_{MN} - C^{(R)}_{MN} . \tag{29}$$

However, it is a straightforward matter to show that the difference matrix of Eq. (29) can be expressed as an integral over only those parts of the unit cell for which $\varphi(x) - \varphi(x') < 0$

$$S_{MN} = \sum_G \frac{1}{k_{Gz}} \int_{\text{uc}} dx\, e^{i(G-M)x} \int_{x_1}^{x_2} dx'\, e^{i(N-G)x} \times \sin\{k_{Gz}[\varphi(x') - \varphi(x)]\} , \tag{30}$$

where the points x_1 and x_2 are the points at which $\varphi(x) - \varphi(x') = 0$ as shown on Fig. 1. (The extension of this procedure to more complicated surface profiles exhibiting several local maxima is straightforward.)

Thus we can write the boundary condition (18) in the form

$$0 = A_M(k_{0z}) + \sum_N (C^{(R)}_{MN} + 2iS_{MN}) F_N . \tag{31}$$

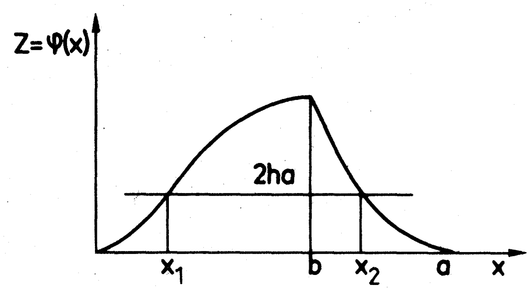

FIG. 1. Single cycle of an arbitrary corrugation profile of period a and amplitude $2ha$. The points x_1 or x_2 are given by the expression $\varphi(x) - \varphi(x_{1,2}) = 0$.

We note that even when both methods lead to exact solutions the matrix S_{MN} is not necessarily the null matrix. This is because there are an infinite number of different source functions which lead to the same diffracted intensities.[14]

A similar result can be presented for the MMM boundary condition.

If the MMM boundary condition (22) is multiplied by $A_{L-M}(k_{Mz})$ and summed on M we are left with the result

$$0 = A_L(k_{0z}) + \sum_N C^{(M)}_{LN} F_N \tag{32}$$

since

$$\sum_M A_{L-M}(k_{Mz}) A'_M = \sum_N A_{L-M}(k_{Mz}), \quad \delta_{M0} = A_L(k_{0z})$$

and

$$C^{(M)}_{LN} = \sum_G \frac{1}{k_{Gz}} A_{L-G}(k_{Gz}) A_{G-N}(-k_{Gz})$$
$$= \sum_G \frac{1}{k_{Gz}} \left(\int_{\text{uc}} dx\, e^{i(G-L)x} e^{-ik_{Gz}\varphi(x)} \right) \times \left(\int_{\text{uc}} dx'\, e^{i(N-G)x'} e^{ik_{Gz}\varphi(x')} \right) . \tag{33}$$

Note that the only differences between this expression and the corresponding matrix in the Rayleigh case of Eq. (27) is the change of signs of k_{Gz} in the exponentials. Again we can obtain the difference between C_{LN} and $C^{(M)}_{LN}$, and in this case it can be expressed in terms of an integral over the part of the corrugation profile for which $\varphi(x) - \varphi(x') > 0$.

$$C_{LN} - C^{(M)}_{LN} = 2iM_{LN} , \tag{34}$$

where

$$M_{LN} = \sum_G \frac{1}{k_{Gz}} \int_{\text{uc}} dx\, e^{i(G-L)x} \left(\int_0^{x_1} dx' + \int_{x_2}^{a} dx' \right) \times e^{i(N-G)x'} \sin\{k_{Gz}[\varphi(x) - \varphi(x')]\} . \tag{35}$$

Thus the boundary condition of Eq. (18) can be written in terms of the MMM matrix as

$$0=A_L(k_{0z})+\sum_N \left(C_{LN}^{(M)}+2iM_{LN}\right)F_N\,. \tag{36}$$

In either case, Eq. (31) or (36), we have the following matrix relation (| | and || || are column and square matrices, respectively)

$$0=|A|+||C+2i\Delta||\;|F_N|$$

or after inversion (and supposing the existence of the inverse matrix)

$$|F_N|=-||1+2iC^{-1}\Delta||^{-1}||C||^{-1}|A|\,. \tag{37}$$

This relation shows clearly that the Fourier component $F_N^{(R)}$ or $F_N^{(M)}$ given, respectively, by the Rayleigh or MMM boundary condition is equal to the first term of an infinite expansion of Eq. (37). This is similar to conserving the first term in a perturbation theory.

IV. COMPARISON WITH CALCULATIONS

To support the arguments presented in Sec. II we have carried out a number of calculations using all three methods of applying the boundary conditions for the case of a triangular corrugation profile. The profile is shown in Fig. 2 and is specified by

$$\varphi(x)=\begin{cases}2hax/b; & 0\le x\le b\\ 2ha(a-x)/(a-b); & b\le x\le a\end{cases}\,, \tag{38}$$

where b is the position of the vertex of the triangle and $2h$, as defined previously, is the total trough to crest amplitude of the corrugation. The results of the calculation for the exact case of applying the boundary conditions at the surface as in Eqs. (18)–(20) are somewhat lengthy and have been presented elsewhere.[8] We will only

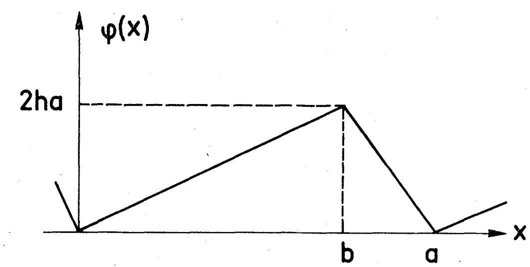

FIG. 2. Triangular profile period a, amplitude $2ha$ with vertex at $x=b$, as defined by Eq. (38).

outline the results here in order to explain why one always obtains a convergent solution.

The question of convergence is important because the inverse C_{NM}^{-1} of the matrix in Eq. (19) does not exist, in the sense that it has elements which become large as the indices N and M become large. However, the diffraction coefficients (20) and hence the scattered intensities are always finite. For the $\varphi(x)$ of Eq. (38) the matrix elements C_{NM} of (19) become small as $1/N^2$ or $1/M^2$ in the limit $|N|$ and $|M|\to\infty$ if $N\ne M$. However, the diagonal elements $N=M$ vary as $1/N$ in the same limit.

Thus in the limit of large $|N|$ or $|M|$ the only important matrix elements are the diagonal terms C_{NN} which become smaller as $1/N$. Consequently in the same limit the only important elements of the inverse C_{NM}^{-1} are the diagonal terms which are proportional to N. In other words the matrix C_{NM} can be thought of as composed of submatrices, where the submatrices of elements with large index values approach either null matrices or diagonal form, with diagonal elements falling off as $1/N$. The inverse C_{NM}^{-1} is then of the same form where for large index values the submatrices are either null or diagonal, with the diagonal elements proportional to N. Thus the defining equation for

TABLE I. Diffraction intensities for helium incident on the triangular profile for several values of h. The beam is incident perpendicularly on the surface ($\Theta_i=0$) and the other parameters of the system are defined by $b=0.75a$ and $ak_0=21.8$, where k_0 is the magnitude of the incident wave vector.

Diffraction order	Angle of diffraction	$h=0.025$	$h=0.05$	$h=0.1$	$h=1.5$
3	62.8°	0.0000	0.0024	0.0038	0.0333
2	36.4°	0.0030	0.0043	0.3795	0.0035
1	17.3°	0.1713	0.5238	0.2959	0.0141
0	0.0°	0.6959	0.1806	0.0743	0.2879
−1	−17.3°	0.0976	0.1475	0.0044	0.5095
−2	−36.4°	0.0280	0.1082	0.0860	0.0913
−3	−62.8°	0.0042	0.0332	0.1562	0.0597
Sum of intensities	(Unitarity)	1.0000	1.0000	1.0000	0.9993

TABLE II. Comparison of the exact, MMM, and Rayleigh boundary conditions for different values of N (for the exact and MMM case N is the number of Fourier components of the source function, while for the Rayleigh case N is the number of diffraction coefficients). The calculations are for the triangular corrugation profile with $h = 0.05$ and all other parameter the same as in Table I.

$h = 0.05$ N	Exact U	MMM U	Rayleigh U
7	0.9997	1.0038	1.0115
9	1.0000	0.9986	1.0082
11	1.0000	0.9989	1.0042
25	1.0000	0.9979	1.0021
51	1.0000	0.9983	1.0003
95	1.0000	1.1005	1.5464
147	1.0000	38.7594	332.5195

the source function (21) becomes for large $|N|$

$$0 = F_N + C_{NN}^{-1} A_N(k_{0z}) . \tag{39}$$

It is seen from Eq. (42) below that $A_N(k_{0z})$ varies as $1/N^2$ for large $|N|$, thus even as $|N| \to \infty$ the F_N are well defined, falling off as $1/N$. The diffraction coefficients given by (20) are also well defined; in the summand A_{G-N} varies as $1/N^2$ for large N and with the above behavior of F_N the series is seen to converge as a sum with terms varying as $1/N^3$.

Calculations have been reported elsewhere for this model[8] and some typical results are given in Tables I and II for a system exhibiting only seven diffracted beams. The calculations appear to give very good results (in the sense that the sum of all intensities is unity and the diffracted intensities are stable) for a wide range of values of h (Ref. 8). (Good results are obtained for values of h as large as 1.5 or greater.)

As shown in the first column of Table II, the results become better and better as the dimension N of the system (18) is increased, in agreement with the convergence arguments above.

Next we discuss the MMM method of applying the boundary conditions, the results of which are given in Eqs. (22) and (23). Inverting Eq. (22) for F_N gives

$$0 = F_N + \sum_M (C'_{NM})^{-1} A'_M \tag{40}$$

and with (23a) this becomes

$$0 = F_N + (C'_{N0})^{-1} . \tag{41}$$

In spite of its simplicity the limiting behavior of C'_{NM} is quite different from that of the corresponding matrix C_{NM} above. For the triangular profile (38) we obtain for C'_{NM} in Eq. (23b)

$$C'_{NM} = \frac{1}{k_{Mz}} A_{N-M}(-k_{Mz}) = \frac{2ha^2(e^{i(N-M)b} e^{ik_{Mz}2ha} - 1)}{[(N-M)b + 2k_{Mz}ha][(N-M)(a-b) - 2k_{Mz}ha]} . \tag{42}$$

Since $k_{Mz} \to +i|M|$ for $|M|$ large it is clear that C'_{MN} varies as $1/N^2$ or $1/M^2$ for large $|N|$ and $|M|$ even when $N = M$.

It can readily be shown that the inverse of an infinite matrix with the behavior of (42) is divergent. The inverse of (42) is defined by the relation

$$\sum_M (C'_{NM})^{-1} C'_{MN'} = \delta_{NN'} . \tag{43}$$

Considering only the diagonal elements of (43), we obtain an inequality by taking the absolute value of each of the matrix elements:

$$\sum_M |(C'_{NM})^{-1}| \, |C'_{MN}| > 1 . \tag{44}$$

We now look at Eq. (44) in the limit of large $|N|$. We replace $|C'_{MN}|$ by the largest element in the column N which in this limit can be written as α/M^2 $(M = N)$. We replace $|(C'_{NM})^{-1}|$ by the largest element in the corresponding row N which is denoted by β. Both of these operations leave the inequality unchanged but have the effect of making the summand independent of M. Since there are M terms in the sum we are left with

$$M\beta(\alpha/M^2) > 1 \tag{45}$$

or

$$\beta > M/\alpha ; \tag{46}$$

that is to say, there is at least one element in the Nth row of $(C'_{NM})^{-1}$ whose magnitude diverges at least as fast as M for large value of M. We note that this proof does not specify which element diverges, and does not rule out the possibility that all elements in the Nth row of $(C'_{NM})^{-1}$ could increase as M for large M. In fact this is quite likely the true behavior since all of the elements in the Nth row of column of C'_{MN} are roughly of the same magnitude in the limit of large $|M|$. Thus the difference between the exact case of Eq. (39) and the MMM condition is that the divergency does not affect just the diagonal elements of the matrix $(C'_{NM})^{-1}$ of Eqs. (40) and (41), but in fact could involve all the elements in the outer rows of the inverse matrix.

If we now examine the F_N coefficient from (41) we see that the above arguments make it plausible that they vary as N for large $|N|$. If this is the case then the summand of Eq. (20) [with $A_{G-N}(k_{Gz})$

given by (42)] will vary as $1/N$ and the summation may give a divergent result for the diffracted-wave coefficient C_G. To prove that the C_G are divergent requires more detailed knowledge of the matrix $(C'_{NM})^{-1}$ [namely, the explicit behavior of $(C'_{N0})^{-1}$], but we have shown that a divergence is possible in this case, whereas with the application of the boundary conditions on the surface the results are definitely convergent.

The numerical results seem to substantiate the above conclusion that the MMM boundary conditions never give convergent results for the triangular corrugation. It appears that reasonably good approximations can be obtained for small h if the matrix equation (22) is truncated at a relatively small dimension; however, if the dimension of the matrix equation is increased the convergence becomes worse. For large values of h convergence cannot be obtained for any dimension. Table II gives a comparison of the MMM result with the exact case of the seven diffracted beam system with $h = 0.05$.

It is seen that the best results occur for a matrix of dimension approximately 25 and for larger dimensions the method fails. When the unitarity is good the intensities of the diffracted beams are nearly the same as in Table I, the differences being within the unitarity defect. Table III compares the calculations for the same system but with different values of h. It is seen that the MMM method does not appear to converge at all when $h \simeq 0.1$ or larger.

The situation of the Rayleigh case can be treated along the same lines as the discussion of the MMM case above. If we solve for the source function using Eq. (26) and (27) we find that the limiting behavior of $C_{MN}^{(R)}$ is similar to $C_{MN}^{(M)}$ above, that is, there are elements in the inverse $(C_{NM}^{R})^{-1}$ that diverge at least as fast as M for large M. Thus we would expect the behavior of the numerical calculations of the Rayleigh case to be roughly the same as for the MMM case.

TABLE III. Comparison of the exact, MMM, and Rayleigh boundary conditions for different amplitudes h of the triangular corrugation profile, all other parameters being the same as in Table I. In all cases the dimension of the system is given by $N = 25$.

h	Exact U	MMM U	Rayleigh U
0.025	1.0000	0.9999	1.0001
0.05	1.0000	0.9979	1.0021
0.075	1.0000	0.9863	1.0229
0.1	1.0000	1.0690	1.1727
0.15	1.0000	154.4187	6.7267

Tables II and III show this to be the case; the results are never convergent and for $h > 0.1$ even approximate results cannot be obtained. We also find that the convergence of the Rayleigh method is substantially worse for large angles of incidence. There is of course no reason why we should expect the Rayleigh method to converge for this corrugation profile since clearly the boundary condition of Eq. (4) cannot in general always be satisfied. There have been other indications, using an entirely different approach, that the Rayleigh method may fail for the case of the triangular corrugation.[13]

V. CONCLUSIONS

We have presented here a discussion of three different methods of solving the corrugated-hard-wall problem: an exact method of applying the boundary conditions on the surface, the application of the boundary conditions on a plane inside the surface (MMM method), and the Rayleigh method. Several calculations have been presented for each of the methods for the particular case of a triangularly corrugated surface.

The application of the boundary conditions on the surface is a necessary and sufficient condition for a solution to the problem and we are able to demonstrate explicitly for the triangle corrugation that the solution converges.

The MMM method of applying the boundary condition $\psi \equiv 0$ below the selvage region of the surface is a necessary condition on the wave function but may not be a sufficient condition (that is, it must be proved for each surface corrugation that it is also a sufficient condition). However, if this method does produce a convergent solution it must be the exact solution according to the uniqueness theorem for the wave equation. Thus we must conclude that either the MMM boundary condition produces the correct solution, or it produces no solution at all (i.e., it diverges). We have shown in Sec. IV that there is reason to suspect that the MMM method diverges for the triangular lattice, and this hypothesis is supported by the numerical calculations.

For strong corrugations the method does not converge at all; while for weak corrugations good approximate results are obtained if the dimension of the system is truncated appropriately, but if the dimension of the system is increased eventually the solution becomes unstable. Garcia and Cabrera have also presented numerical results which seem to indicate that the MMM method does not converge for a variety of other corrugation profiles as well, especially in the case of large-amplitude corrugation.[4]

The Rayleigh method is in a slightly different category from the other two since it consists of extending the asymptotic form of the wave function up to the surface and then applying the boundary condition. Thus in general, the Rayleigh condition is not even a necessary condition on the wave function and it must be proved in each application that it can produce a solution. (Proof of a solution has been shown only for the case of a sinusoidal profile of small amplitude). Similar to the MMM case, the calculations presented here seem to indicate that the Rayleigh method is not convergent for the triangular profile. The numerical calculations of Garcia and Cabrera have pointed out difficulties involved with a number of other profiles.

We conclude that if one of these methods produces a solution it must clearly be the correct solution. The fundamental question is to show that the method produces a convergent solution.

As a final note we would like to point out again that even under conditions in which the MMM or Rayleigh methods may not be strictly convergent they can often be made to give reasonably approximate results by suitable truncation. This could be an important point from the standpoint of numerical calculations because these two methods are very fast. The exact method of applying the boundary conditions on the surface is substantially slower because of the intermediate summation over G in Eq. (19). On the other hand, with the numerical procedure developed by Garcia and Cabrera the calculation is relatively fast and easy to handle and consequently it would be preferable to use the exact condition.

ACKNOWLEDGMENTS

We would like to thank Dr. D. Degras and Dr. C. Manus for their encouragement during this work and for a critical reading of the manuscript. We would also like to thank Dr. J. Lapujoulade for many helpful discussions.

---

*Permanent address: Dept. of Physics and Astronomy, Clemson University, Clemson, S.C. 29631.

[1] J. W. Strutt (Lord Rayleigh), Proc. R. Soc. London Ser. A 79, 399 (1907). *The Theory of Sound* (Dover, New York, 1945), Vol. II.

[2] F. Toigo, A. Marvin, V. Celli, and N. R. Hill, Phys. Rev. B 15, 5618 (1977).

[3] N. Garcia and N. Cabrera, in *Proceedings of the Third International Conference on Solid State Surfaces, Vienna, 1977*, edited by R. Dobrozemsky *et al.* (Vienna, 1977), Vol. I. p. 379.

[4] N. Garcia and N. Cabrera (unpublished).

[5] N. Garcia, J. Chem. Phys. 67, 897 (1977).

[6] N. Garcia and J. Lapujoulade (unpublished).

[7] R. I. Masel, R. P. Merrill, and W. H. Miller, Phys. Rev. B 12, 5545 (1975).

[8] G. Armand and J. R. Manson, Phys. Rev. B 18, 6510 (1978).

[9] A. Messiah, *Mécanique Quantique* (Dunod, Paris, 1965), Vol. 1, p. 83.

[10] R. Petit and M. Cadilhac, C. R. Acad. Sci. B 262, 468 (1966).

[11] R. F. Millar, Proc. Camb. Philos. Soc. 65, 773 (1969).

[12] L. I. Schiff, *Quantum Mechanics*, 3rd ed. (McGraw Hill, New York, 1968), p. 32.

[13] N. R. Hill and V. Celli (unpublished).

[14] J. L. Beeby, J. Phys. C 9, L377 (1976).