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## Spectrum of Density Fluctuations in Gases

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The spectrum of density fluctuations in a simple gas is calculated by solving the linearized Boltzmann equation as an initial-value problem. The analysis is based on the method of polynomial expansion and on the use of generalized kinetic models. The numerical convergence of both types of solutions is studied, and it is shown that the method of kinetic models is capable of giving very accurate solutions to the Boltzmann equation at any wavelength to mean-free-path ratio. Explicit results are obtained for two repulsive interactions, the rigid-sphere potential and the Maxwell molecule potential. It is found that density fluctuations are not very sensitive to the details of the repulsive part of the intermolecular interaction.

### I. INTRODUCTION

It is well known that the molecular description of many processes and phenomena of interest in kinetic theory begins at the level of the linearized Boltzmann equation. For explicit calculations, however, this equation is sufficiently intractable that instead most investigators have used simplified kinetic-model descriptions. The model solutions have proved to be exceedingly useful in both formal analysis and physical applications, but little is known about their convergence in a quantitative sense. The purpose of this paper is to present certain types of solutions to the Boltzmann equation in the context of a specific initial-value problem. The results, which are obtained numerically, are useful for two reasons: they enable us to discuss the accuracy of commonly used kinetic models and their extensions, and they provide a means of studying the effects of different interaction force laws.

The initial-value problem with which we are concerned is the linear-density response of a gas to a microscopic-density impulse, and physically it is related to the problem of time-dependent density

fluctuations in the gas at equilibrium. The connection between fluctuations and response is a consequence of general statistical mechanical principles<sup>1</sup>; in the present application it leads to an unambiguous relation<sup>2</sup> between density fluctuations and the linearized Boltzmann equation.

Studies of density fluctuations in gases have been carried out using kinetic equations which are approximations to the linearized Boltzmann equation.<sup>3-6</sup> An attempt was also made to derive results directly from the Boltzmann equation for Maxwell molecules.<sup>6</sup> A method of polynomial expansion was used in the calculation; consequently, the procedure is not useful at small wavelength to mean-free-path

<sup>1</sup> H. B. Callen and T. A. Welton, *Phys. Rev.* **83**, 34 (1951); R. Kubo, in *Lectures in Theoretical Physics* (Interscience Publishers, Inc., New York, 1959), Vol. I, Chap. 4.

<sup>2</sup> J. M. J. van Leeuwen and S. Yip, *Phys. Rev.* **139**, A1138 (1965).

<sup>3</sup> S. Yip and M. Nelkin, *Phys. Rev.* **139**, A1241 (1964).

<sup>4</sup> S. Yip and S. Ranganathan, *Phys. Fluids* **8**, 1956 (1965).

<sup>5</sup> E. P. Gross, *Phys. Rev.* **158**, 146 (1967).

<sup>6</sup> S. Ranganathan and S. Yip, *Phys. Fluids* **9**, 372 (1966).

The matrix elements of  $C_P$  in the Appendix of this paper are not correct; the factors  $25\gamma_2$ ,  $37\gamma_3$ ,  $155\gamma_4$ ,  $-368\gamma_2$ , should be replaced by  $17\gamma_2$ ,  $29\gamma_3$ ,  $58\gamma_4$ ,  $-68\gamma_2$ , respectively.

ratios. In the present work we have extended the previous kinetic model calculations to arbitrary order for Maxwell molecules, and have formulated similar calculations for rigid-sphere molecules. Exact solutions to kinetic-model equations of arbitrary order have been obtained, and the numerical convergence of these solutions at sufficiently high order has been established. In the region where the expansion method also gives numerically converged solutions, the two methods of calculations give identical results. We can, therefore, conclude that the kinetic-model approach provides an extremely accurate means of solving the linearized Boltzmann equation at any wavelength to mean-free-path ratio. Moreover, it seems reasonable to regard the converged model solutions as exact solutions to the Boltzmann equation.

The initial-value problem of density fluctuations is formulated in the next section where both methods of calculation, the expansion of distribution function, and the use of kinetic models are discussed. Maxwell molecules and rigid-sphere molecules are then treated explicitly. In comparing the solutions for different potentials the calculations can be made consistent by adjusting the force constant in the Maxwell potential and the rigid-sphere diameter to give the same value of shear viscosity. Numerical results are presented which permit quantitative estimates of error in the low-order kinetic model solutions. They also enable us to conclude that density fluctuations are rather insensitive to the details of the repulsive interaction. A number of remarks are given in the last section.

## II. THE SPECTRUM OF DENSITY FLUCTUATIONS, $S(\mathbf{k}, \omega)$

The phenomenon of time-dependent fluctuations in an equilibrium system is most appropriately described by the correlation function  $G(\mathbf{r}, t)$  first introduced by van Hove<sup>7</sup> in the theory of neutron scattering. Our main concern here is to study the spectrum of density fluctuations in a dilute, monatomic gas. The spectrum  $S(k, \omega)$ , is defined as the space-time Fourier transform of  $G(r, t)$ . Because of translational and rotational symmetry  $G$  and  $S$  are functions only of the magnitude of  $\mathbf{r}$  and  $\mathbf{k}$ , respectively. We also consider only classical systems in which case  $G$  is even in  $t$  and  $S$  even in  $\omega$ . Thus,

$$S(k, \omega) = 2 \operatorname{Re} \int_0^\infty dt \int d^3r e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} G(r, t). \quad (1)$$

It has been shown that  $G(r, t)$  can be obtained from a kinetic equation, and that this equation reduces to the linearized Boltzmann equation when incomplete collision effects are ignored.<sup>2</sup> It is, therefore, implied in using this description that variations on the time scale comparable to a collision duration (typically  $10^{-13}$  sec) are of no interest. For a rigid-sphere intermolecular potential this is not a restriction. The fundamental equation to be solved is, therefore, well known<sup>8</sup>:

$$\left( \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \right) f(\mathbf{r}, \mathbf{v}, t) = J(f), \quad (2)$$

$$J(f) = n_0 \int d\Omega \int d^3v_1 f_0(\mathbf{v}_1) |\mathbf{v} - \mathbf{v}_1| I(\theta, |\mathbf{v} - \mathbf{v}_1|) \cdot [f(\mathbf{v}') + f(\mathbf{v}_1') - f(\mathbf{v}) - f(\mathbf{v}_1)], \quad (3)$$

and the initial condition to be used is a localized density impulse

$$f(\mathbf{r}, \mathbf{v}, t = 0) = \delta(\mathbf{r}). \quad (4)$$

In Eqs. (2) and (3),  $n_0$  is the equilibrium number density,  $f_0(\mathbf{v})$  the absolute Maxwellian  $(2\pi v_0^2)^{-3/2} \exp(-v^2/2v_0^2)$ ,  $v_0^2 = k_B T/m$ , and  $I(\theta, |\mathbf{v} - \mathbf{v}_1|)$  is the binary collision cross section.

The connection between density fluctuations and the initial-value problem is given by<sup>3</sup>

$$G(r, t) = \int d^3v f_0(\mathbf{v}) f(r, \mathbf{v}, t). \quad (5)$$

It is generally more convenient to consider the transformed equation directly:

$$(i\omega - i\mathbf{k} \cdot \mathbf{v}) f(k, \mathbf{v}, \omega) = J[f(k, \mathbf{v}, \omega)] + 1, \quad (6)$$

where

$$f(k, \mathbf{v}, \omega) = \int_0^\infty dt \int d^3r e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} f(r, \mathbf{v}, t) \quad (7)$$

since the real part of the velocity integral of

$$f_0(\mathbf{v}) f(k, \mathbf{v}, \omega)$$

gives  $S(k, \omega)$ .

Two methods, both involving a successive approximation procedure, will be used to obtain solutions to Eq. (6). The method of distribution function expansion is due to Wang Chang and Uhlenbeck.<sup>9</sup>

<sup>8</sup> G. E. Uhlenbeck and G. W. Ford, *Lectures in Statistical Mechanics* (American Mathematical Society, Providence, Rhode Island, 1963), Chaps. IV and VI.

<sup>9</sup> C. S. Wang Chang and G. E. Uhlenbeck, University of Michigan Engineering Research Institute ONR Contract N60nr-23222 (1952).

<sup>7</sup> L. van Hove, *Phys. Rev.* **95**, 249 (1954).

In terms of a complete, orthonormal set of functions  $\{\psi_i\}$  one writes

$$f(k, \mathbf{v}, \omega) = \sum_i a_i(k, \omega) \psi_i(\mathbf{v}), \quad (8)$$

where  $a_i$  is the scalar product

$$a_i(k, \omega) = (\psi_i, f). \quad (9)$$

Equation (6) then becomes

$$\sum_i a_i(k, \omega) [(i\omega - ikv_z) \psi_i(\mathbf{v}) - \sum_\alpha J_{i\alpha} \psi_\alpha(\mathbf{v})] = 1, \quad (10)$$

where

$$J_{i\alpha} \equiv (\psi_\alpha, J[\psi_i]) = J_{\alpha i} \quad (11)$$

and the  $z$  direction is taken along  $\mathbf{k}$ . If the expansion is simply terminated, i.e., at  $j = N$ , a finite set of simultaneous equations results, after forming scalar products with  $\psi_n$ :

$$i\omega a_n - \sum_i^N a_i (ikV_{in} + J_{in}) = (\psi_n, 1) \quad (12)$$

with  $V_{in} = (\psi_n, v_z \psi_i)$ . These can readily be solved for the coefficient  $a$ 's and the procedure can be repeated for successively larger  $N$ 's until the computed values of  $S(k, \omega)$  converge.

The basic advantage of kinetic models<sup>10</sup> is that they are capable of describing the hydrodynamic and Knudsen regions properly, and between these limits the solutions should represent reasonable interpolations. It is reasonable to assume that higher-order model descriptions should give finer results; however, the convergence of this method has not been numerically studied. The  $M$ th order kinetic model consists of taking<sup>10,11</sup>

$$J[f] \cong \sum_{\alpha, i=1}^M a_\alpha (J_{\alpha i} + \lambda \delta_{\alpha i}) \psi_i - \lambda f. \quad (13)$$

We follow an earlier convention<sup>10</sup> by taking  $\lambda = |J_{M+1, M+1}|$ . With the substitution of Eq. (13), Eq. (6) becomes

$$(i\omega - ikv_z + \lambda) f(k, \mathbf{v}, \omega) = 1 + \sum_{\alpha, i=1}^M a_\alpha(k, \omega) B_{\alpha i} \psi_i(\mathbf{v}), \quad (14)$$

where

$$B_{\alpha i} = J_{\alpha i} + \lambda \delta_{\alpha i}. \quad (15)$$

The set of integral equations is easily reduced to algebraic form by using the notation introduced in Eq. (9). Thus,

$$\sum_{\alpha=1}^M a_\alpha(k, \omega) \left[ \delta_{\alpha n} - \sum_{i=1}^M B_{\alpha i} \left( \psi_n, \frac{\psi_i}{i\omega - ikv_z + \lambda} \right) \right] = \left( \psi_n, \frac{1}{i\omega - ikv_z + \lambda} \right). \quad (16)$$

### III. MAXWELL MOLECULES

When the intermolecular force law is of the form  $F(r) = \chi/r^5$ , the scattering cross section  $I(\theta, |\mathbf{v} - \mathbf{v}_1|)$  becomes inversely proportional to the relative speed. This is the only case for which the linearized Boltzmann collision operator has been studied completely analytically.<sup>9</sup> We denote the eigenfunctions using the same normalization by  $\psi_{r,l}$  as in Ref. 12. The spectrum of eigenvalues  $\lambda_{r,l}$  is known to be an infinite, purely discrete set. An extensive table of their values has been compiled by Alterman *et al.*<sup>13</sup> To apply the methods discussed in Sec. II it will be necessary to replace the double subscripts ( $r, l$ ) by a single index  $j$ . Two methods suggest themselves,<sup>12</sup> depending on whether the ordering is to be based on the magnitude of the eigenvalues ( $\lambda$  ordering) or on the polynomial degree in the eigenfunctions ( $p$  ordering). For the polynomial expansion method (Wang Chang-Uhlenbeck) a general expression for  $V_{jn}$  is needed. This has been derived by Mott-Smith.<sup>14</sup>

Introducing the dimensionless variables

$$x = \omega/\sqrt{2} kv_0, \quad y = |\lambda_{1,1}|/\sqrt{2} kv_0,$$

from Eq. (12) we obtain

$$\begin{aligned} \left( ix + \frac{\lambda_n}{\lambda_{1,1}} y \right) a_n - i \left\{ l \left[ \frac{r+l+\frac{1}{2}}{(2l+1)(2l+1)} \right]^{\frac{1}{2}} a_n \right. \\ \left. - l \left[ \frac{r+1}{(2l+1)(2l-1)} \right]^{\frac{1}{2}} a_n \right. \\ \left. + (l+1) \left[ \frac{r+l+\frac{3}{2}}{(2l+1)(2l+3)} \right]^{\frac{1}{2}} a_n \right. \\ \left. - (l+1) \left[ \frac{r}{(2l+1)(2l+3)} \right]^{\frac{1}{2}} a_n \right\} \\ = \frac{1}{kv_0\sqrt{2}} \delta_n, \end{aligned} \quad (17)$$

<sup>12</sup> L. Sirovich, *Phys. Fluids* **6**, 10 (1963).

<sup>13</sup> Z. Alterman, K. Frankowski, and C. L. Pekeris, *Astro-phys. J. Suppl.* **7**, 291 (1962).

<sup>14</sup> H. M. Mott-Smith, Massachusetts Institute of Technology, Lincoln Laboratory Group Report V-2 (1954).

<sup>10</sup> E. P. Gross and E. A. Jackson, *Phys. Fluids* **2**, 432 (1959).

<sup>11</sup> L. Sirovich, *Phys. Fluids* **5**, 908 (1962).

where the various indices are related according to

$$\begin{aligned} n &= (r, l), & n_1 &= (r, l - 1), \\ n_2 &= (r + 1, l - 1), & n_3 &= (r, l + 1), \\ n_4 &= (r - 1, l + 1). \end{aligned}$$

With either ordering,

$$S(x, y) = 2 \operatorname{Re} [a_1(x, y)]. \quad (18)$$

Application of the kinetic-model method requires the determination of the scalar products in Eq. (16). General expressions for these are given in Appendix A.<sup>15</sup> By expressing velocity and time in units of  $v_0$  and  $\lambda^{-1}$ , respectively, we find from Eq. (14)

$$\begin{aligned} (\Lambda - i\xi_z)f(k, \xi, \omega) \\ = \sqrt{2} y^* \sum_{i=1}^M a_i(k, \omega) \beta_{ii} \psi_i(\xi) + (kv_0)^{-1}, \end{aligned} \quad (19)$$

where

$$y^* = \lambda/kv_0\sqrt{2}, \quad \Lambda = \sqrt{2}(ix + y^*), \quad \beta_{ii} = \lambda^{-1}J_{ii} + 1.$$

As a result, Eq. (16) becomes

$$a_n(x, y) = \frac{1}{\lambda} \gamma_{1n} + \sum_{i=1}^M a_i(x, y) \beta_{ii} \gamma_{in}, \quad (20)$$

where

$$\gamma_{in} \equiv \sqrt{2} y^* \int d^3\xi \frac{\psi_i(\xi) \psi_n(\xi) f_0(\xi)}{\Lambda - i\xi_z} \quad (21)$$

and the closed form expression for  $\gamma_{in}$  is to be found in Appendix A. The spectrum of density fluctuations is now determined from Eqs. (18) and (20). Notice that  $y^*$  is model-dependent whereas  $y$  depends on  $k$ ,  $v_0$ , and the force constant  $\chi$ .

For explicit calculations it is necessary to know the absolute magnitude of the eigenvalues which are specified by  $\chi$  for a particular gas. A way of determining this constant is to require that the transport coefficients derived from the Boltzmann equation agree with the measured values. Since the Maxwell molecule potential gives the correct Eucken ratio,<sup>8</sup> one can specify  $y$  in terms of either the shear viscosity or the thermal conductivity. We will use the viscosity  $\eta$  because it is generally a more precisely measured quantity. The relation between  $\eta$  and one of the eigenvalues is<sup>8</sup>

$$|\lambda_{0,2}| = \rho v_0^2 / \eta, \quad (22)$$

where  $\rho$  is the mass density. Since the ratio of  $\lambda_{1,1}$  to  $\lambda_{0,2}$  is  $\frac{2}{3}$ , we have

$$y = \frac{\sqrt{2}}{3} \frac{\rho v_0}{\eta k}. \quad (23)$$

#### IV. RIGID-SPHERE MOLECULES

Mott-Smith<sup>14</sup> has derived the general expression for the matrix elements  $J_{\alpha i}$  using the Maxwell molecule eigenfunctions  $\psi_{r,i}$ . Recently, a method for obtaining similar matrix elements for any repulsive force law has been developed by Ford.<sup>16</sup> The sound problem has been treated with rigid-sphere kinetic models,<sup>15,17</sup> and in this work a large block of  $J_{\alpha i}$  was computed. The relevant results for the present calculation are summarized in Appendix B. These are included here to avoid confusion in normalization factors and to make clear the explicit connection between  $y$  and the transport coefficients.

The fourth-order expression for the shear viscosity of a rigid-sphere gas is<sup>18</sup>

$$\eta = \frac{5.08}{16} \left( \frac{k_b m T}{\pi} \right)^{\frac{1}{2}} \frac{1}{d^2}, \quad (24)$$

where  $d$  is the hard-core diameter. We define  $y$  as

$$y = |J_{02,02}| / kv_0 \sqrt{2} \quad (25)$$

and so

$$y^* = y |J_{M+1, M+1}| / |J_{02,02}|. \quad (26)$$

Combining this with the expression for  $J_{02,02}$  from Appendix B we find

$$y = 0.508 \sqrt{2} \frac{\rho v_0}{\eta k}. \quad (27)$$

The result can be compared with Eq. (23). The ratio of rigid-sphere to Maxwell molecule  $y$  values is seen to be 1.52. This result is essentially the same if we had used the thermal conductivity.

#### V. NUMERICAL RESULTS

It can be seen from the remarks made in Sec. II that the polynomial expansion method (Wang Chang-Uhlenbeck) should give rapidly convergent results at large  $y$ , the parameter which is a measure of the wavelength to mean-free-path ratio. As  $y$  decreases the results obtained with a particular

<sup>16</sup> G. W. Ford (private communication).

<sup>17</sup> L. Sirovich and J. K. Thurber, *J. Acoust. Soc. Am.* **37**, 329 (1965).

<sup>18</sup> S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, New York 1953), Chaps. 7-10.

<sup>15</sup> L. Sirovich and J. K. Thurber, in *Rarefied Gas Dynamics*, J. H. de Leeuw, Ed. (Academic Press Inc., New York, 1965), Vol. 1, p. 21. In this paper, Eq. (F.2) contains a number of misprints; also, in Table II  $B_{20,30}$  should have a positive sign.

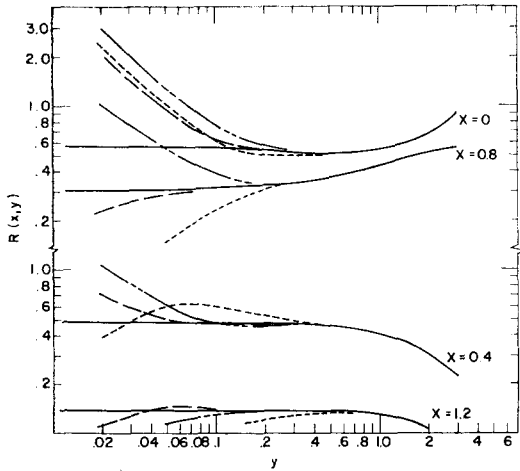


FIG. 1. The behavior of  $S(k, \omega)$  for Maxwell molecules as a function of wavelength to mean-free-path ratio. Results are given as  $R(x, y) = kv_0 S(x, y) / \sqrt{2} \pi$ , with  $x = \omega / \sqrt{2} kv_0$  and  $y = \lambda_{1,1} / \sqrt{2} kv_0$ . Various orders of truncation in the polynomial expansion method are shown,  $N = 30$  (---),  $N = 46$  (-·-·-),  $N = 60$  (—). Also shown is the kinetic model result (—) for  $M = 21$ .

truncation order (fixed  $N$ ) would diverge, the value of  $y$  where this occurs decreases with increasing  $N$ . The general behavior is depicted in Fig. 1, where the variation of the dimensionless function  $2kv_0 S(x, y)$  for Maxwell molecules is shown for several values of  $x$ . The kinetic model results used for this comparison correspond to the solutions with  $M = 21$ . As we will see, from a numerical point of view the latter results can be regarded as convergent, and it is, therefore, plausible to regard them as exact.

Even though the kinetic models are capable of interpolating between correct asymptotic limits, the accuracy and rate of convergence of these descriptions in the transition region ( $y$  around unity) have yet to be investigated in detail. Ranganathan and Yip<sup>6</sup> have considered the models with  $M = 5$  in computing  $S(k, \omega)$ , and Sirovich and Thurber<sup>17</sup> have employed models with  $M \leq 11$  in their analysis of sound propagation experiments. We have obtained  $S(k, \omega)$  for successively larger  $M$  until numerical convergence is achieved. The results for Maxwell molecules are given in Figs. 2 and 3. As expected, the convergence is less rapid at intermediate values of  $y$ . At  $y = 5$  (not shown) there is essentially no change beyond  $M = 9$ . In all the cases examined,  $M = 21$  is found to be sufficient to insure complete convergence at any  $x$ . Although both  $p$ -ordering and  $\lambda$ -ordering solutions converge to the same values as they must, the superiority of  $\lambda$  ordering is clearly displayed in Fig. 3.

Kinetic model solutions have also been obtained for rigid-sphere molecules. A similar study of their

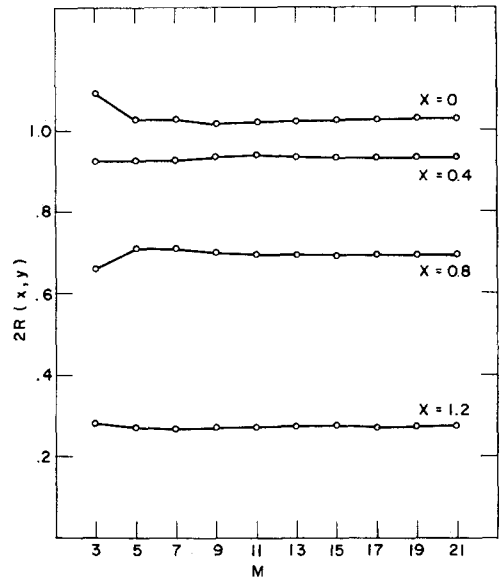


FIG. 2. Convergence of  $R(x, y)$  for Maxwell molecules as a function of kinetic model order  $M$  for  $y = 0.4$ . The open circles denote the results obtained with eigenvalue ordering and they are simply joined by straight lines.

convergence is shown in Fig. 4. Convergence rate is generally slower compared with the case of Maxwell molecules, especially at small values of  $x$ . The comparison of Maxwell molecule and rigid-sphere results provides a systematic means of studying the

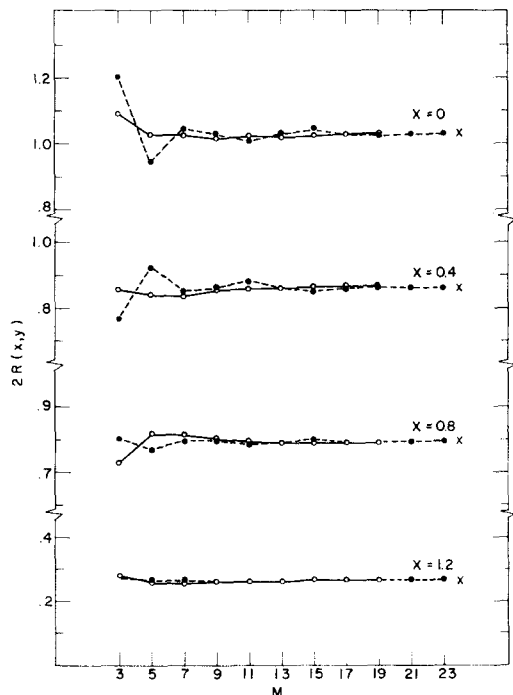


FIG. 3. Same as Fig. 2 for  $y = 0.78$ . Also shown are the results from polynomial ordering (closed circles) and those obtained with the polynomial expansion method (crosses) for  $N = 46$ .

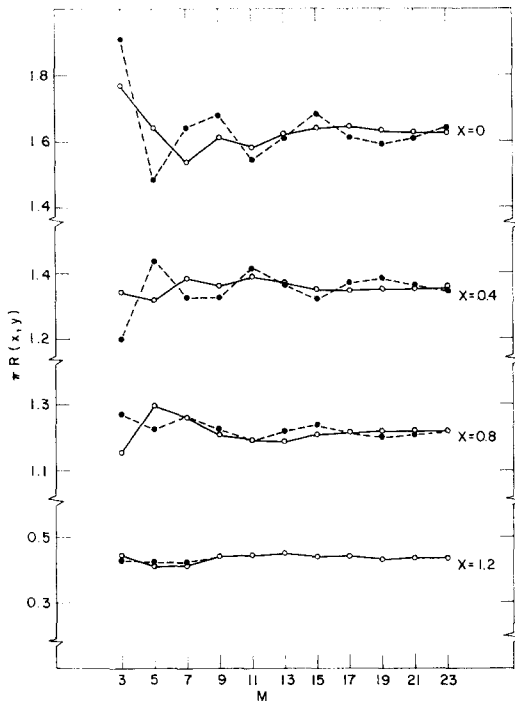


FIG. 4. Convergence of  $R(x, y)$  for rigid-sphere molecules as a function of  $M$ . Value of  $y$ , now defined by Eq. (25), is 1.2275. Polynomial and eigenvalue ordering results are denoted by closed and open circles, respectively.

quantitative effects of different interaction potentials. To be consistent one only needs to use corresponding  $y$  values according to Eqs. (23) and (27). Table I contains the numerically converged kinetic model solutions. The maximum deviation between the  $1/r^4$  and rigid-sphere potentials is seen to be about 3%.

## VI. DISCUSSION

We have investigated two methods for computing the spectrum of density fluctuations for a dilute gas. Although both methods are capable of giving accurate solutions to the linearized Boltzmann equation, the kinetic model approach is preferable because it provides an effective interpolation procedure which is valid at any ratio of wavelength to mean free path. Our results indicate that in a quantitative calculation of  $S(k, \omega)$ , a high-order ( $M \geq 21$ ) model equation possesses essentially the same physical content as the linearized Boltzmann equation. The former is obviously much more tractable.

The fact that fine details of the collision cross section are not clearly reflected in  $S(k, \omega)$ , is indicated by the present comparison of results for the Maxwell and rigid-sphere molecules. A general expression for the  $J$  matrix for any repulsive force law

is now available,<sup>16</sup> and in principle, the corresponding  $S(k, \omega)$  can be computed. The results, however, are not expected to be very different from those given here since Maxwell and rigid-sphere molecules represent the limits of soft and hard potentials for a neutral gas. It is clear that we can only conclude that  $S(k, \omega)$  is not very sensitive to the shape of the repulsive potential because the effects of attractive interaction are still unknown. The computational problem for a two-body potential with an attractive tail is more difficult, but would be worthwhile studying when very precise determination of  $S(k, \omega)$  (e.g., light scattering) becomes available. It has been proposed that light scattering be used as a means of testing the Boltzmann equation; in this application our results provide a quantitative basis for the interpretation of recent experiments.<sup>19</sup>

It is generally recognized that sound propagation and light scattering are closely related phenomena. In the long wavelength region it is easy to see their connection in terms of the dispersion relation. In the kinetic region, where the presence of a source in the sound problem has to be treated explicitly, the relationship is less clear. The Maxwell molecule and rigid-sphere potentials have also been used in the calculation of sound speed and attenuation.<sup>15,17</sup> The variations due to the difference in potentials are more pronounced than those observed in Table I.

Finally, we mention that the present method of calculations can also be applied to general response and correlation functions involving any macroscopic variable. The formalism most appropriate for this type of investigation has been developed by Martin.<sup>20</sup> Although only preliminary calculations have been considered,<sup>6</sup> it appears that such studies should lead to detailed information about the frequency and wavelength dependence of transport coefficients.

## ACKNOWLEDGMENTS

One of us (S.Y.) would like to acknowledge discussions with S. Ranganathan prior to the initiation of this work.

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<sup>19</sup> A. Sugawara, S. Yip, and L. Sirovich, Phys. Rev. (to be published).

<sup>20</sup> L. P. Kadanoff and P. C. Martin, Ann. Phys. (N. Y.) 24, 419 (1963); P. C. Martin, in *Statistical Mechanics of Equilibrium and Non-Equilibrium*, J. Meixner, Ed. (North-Holland Publishing Company, Amsterdam, 1965), p. 100.

TABLE I. Values of  $2R(x,y)$  for rigid-sphere and Maxwell molecules. Ratio of  $y$  values for the two cases is 1.524 and is determined by using Eqs. (23) and (27).

$x$	Rigid sphere $y = 3.0$	Maxwell $y = 1.9685$	Rigid sphere $y = 2.0$	Maxwell $y = 1.3123$
0.0	1.3347	1.3579	1.1282	1.1414
0.1	1.1787	1.1826	1.0693	1.0721
0.2	0.90579	0.89048	0.94196	0.92875
0.3	0.70990	0.69199	0.82303	0.80407
0.4	0.61051	0.59703	0.74851	0.73334
0.5	0.58808	0.58164	0.72471	0.71907
0.6	0.63790	0.64111	0.74993	0.75792
0.7	0.77538	0.79368	0.81710	0.84109
0.8	1.0067	1.0428	0.89138	0.92443
0.9	1.1375	1.1581	0.87358	0.89076
1.0	0.82178	0.80428	0.68495	0.67537
1.1	0.42609	0.41135	0.43628	0.42108
1.2	0.21353	0.20720	0.25431	0.24490
1.3	0.11466	0.11231	0.14813	0.14378
1.4	0.066460	0.065688	0.089188	0.087515
1.5	0.041069	0.040912	0.055886	0.055440

$x$	Rigid sphere $y = 1.17$	Maxwell $y = 0.767$	Rigid sphere $y = 0.5$	Maxwell $y = 0.32808$
0.0	1.0326	1.0305	1.0487	1.0378
0.1	1.0138	1.0093	1.0379	1.0308
0.2	0.96731	0.95848	1.0103	1.0109
0.3	0.91379	0.90336	0.97528	0.98037
0.4	0.86968	0.86224	0.93811	0.94112
0.5	0.84130	0.84087	0.89621	0.89344
0.6	0.82529	0.83416	0.84143	0.83543
0.7	0.80888	0.82617	0.76654	0.76402
0.8	0.77015	0.78977	0.67183	0.67724
0.9	0.68642	0.69865	0.56580	0.57689
1.0	0.55586	0.55580	0.45964	0.46984
1.1	0.40791	0.40010	0.36164	0.36596
1.2	0.27820	0.26958	0.27599	0.27409
1.3	0.18246	0.17634	0.20423	0.19902
1.4	0.11823	0.11484	0.14663	0.14130
1.5	0.076918	0.075440	0.10255	0.098813

APPENDIX A

In this appendix we summarize the results for calculating  $\gamma_{\nu j}$ . We begin with the expression given in Ref. 15 [Eq. (B.15)]. In the present notation

$$\gamma_{\nu j} = \sqrt{2} y^* C_{r l, r' l'} \sum_{j=0}^r \sum_{j'=0}^{r'} \sum_{k=0}^{[l/2]} \sum_{k'=0}^{[l'/2]} \Gamma_{r l r' l'}^{i k j' k'} \cdot I_{r+r'+k+k'-j-j', l+l'-2(k+k')}, \tag{A1}$$

where  $\nu = (r, l)$  and  $j = (r', l')$

$$C_{r l, r' l'} = \frac{(-)^{r+r'} (1)_{2l} (1)_{2l'}}{2^{\frac{1}{2}(l+l'+1)} \{(1)_l (1)_{l'}\}^2} \cdot \left[ \frac{(2l+1)(2l'+1)}{(1)_r (1)_{r'} (\frac{1}{2})_{r+l+1} (\frac{1}{2})_{r'+l'+1}} \right]^{\frac{1}{2}}, \tag{A2}$$

$$\Gamma_{r l r' l'}^{i k j' k'} = (-)^{i+i'+k+k'} 2^{i+j'-r-r'-2(k+k')} \frac{(r-j+1)_i}{(1)_i} \cdot \frac{(r'-j'+1)_{j'}}{(1)_{j'}} \frac{(l-2k+1)_{2k}}{(1)_k} \frac{(l'-2k'+1)_{2k'}}{(1)_{k'}}$$

$$\frac{(r+l+\frac{3}{2}-j)_j (r'+l'+\frac{3}{2}-j')_{j'}}{(l+\frac{1}{2}-k)_k (l'+\frac{1}{2}-k')_{k'}}. \tag{A3}$$

The quantity  $I_{m,n}$  is defined by

$$I_{m,n} = (1)_m \sum_{p=0}^m \frac{2^{m-p}}{(1)_p} I_{n+2p} \sum_{q=0}^{m-p} \frac{(\frac{1}{2})_q (\frac{1}{2})_{m-p-q}}{(1)_q (1)_{m-p-q}} \tag{A4}$$

and

$$I_n = i A_{n-1} - i \Delta I_{n-1}, \tag{A5}$$

where  $A_n = 2^{n/2} (\frac{1}{2})_{n/2}$  for  $n = \text{even}$ , otherwise, it is zero, and

$$I_0 \equiv \frac{i}{\sqrt{2}} W\left(\frac{\Lambda}{i\sqrt{2}}\right). \tag{A6}$$

The plasma dispersion function<sup>21</sup>  $W(z)$  is defined by

$$W(z) \equiv \frac{1}{\pi^{\frac{1}{2}}} \int_{-\infty}^{\infty} \frac{e^{-t^2}}{t-z} dt. \tag{A7}$$

<sup>21</sup> B. D. Fried and S. D. Conte, *The Plasma Dispersion Function* (Academic Press Inc., New York, 1961), p. 1.

The symbol  $(b)_m$  is the Barnes symbol which means

$$(b)_m \equiv b(b + 1) \cdots (b + m - 1)$$

and  $[l/2]$  is Gauss' symbol denoting the largest integer which does not exceed  $l/2$ .

**APPENDIX B**

Here we give the matrix elements  $J_{ij}$ , defined by Eq. (11) for rigid-sphere molecule. In this case

$$J_{ij} = n_0 v_0 \int d^3\xi \psi_i(\xi) f_0(\xi) \int d\Omega \int d^3\xi_1 f_0(\xi_1) I(\theta, |\xi - \xi_1|) |\xi - \xi_1| \cdot \{ \psi_i(\xi_1) + \psi_i(\xi') - \psi_i(\xi_1) - \psi_i(\xi) \}, \tag{B1}$$

where  $\psi_i(\xi)$  is the Maxwell molecule eigenfunction given in Ref. 12. Using the result derived by Mott-

Smith<sup>14</sup> [his Eq. (41)], we obtain

$$J_{ij} = -n_0 v_0 \delta_{il} \pi d^2 \left[ \frac{r! r'! (2l + 1)(2l' + 1)}{\Gamma(r + l + \frac{3}{2}) \Gamma(r' + l' + \frac{3}{2})} \right]^{\frac{1}{2}} \frac{(2l)!}{\Gamma(l + \frac{3}{2})} \frac{1}{2^{r+r'+3l}} \sum_{n=0}^{\min(r, r')} \sum_{m=0}^l \frac{4^n \Gamma(l - m + r + r' - 2n - \frac{1}{2})}{(l - m)! (r - n)! (r' - n)!} B_m^n, \tag{B2}$$

where

$$B_m^n = \frac{(m + 2n + 1)!}{(2n + 1)! m!} - \frac{2^{m-1} (m + n + 1)!}{n! m!}, \tag{B3}$$

$$B_0^0 = 0,$$

and  $i = (r, l), j = (r', l')$ ,  $d$  is the diameter of the rigid sphere. Eq. (B2) differs from that of Mott-Smith in the normalization of  $\psi_i$  and in the definition of dimensionless velocity variable.