

the presently investigated multiplets, the results of this experiment should be regarded as superseding his and Foster's values.

For all multiplets except the one at 4368 Å the spread between the most recent theoretical and experimental results, namely those of Bates and Damgaard, Kelly, Vainshtein, Buttrey and Gibson, Doherty and this experiment, does not exceed 26%. One of the rare cases is encountered, where the agreement between several independent methods is so good that one may consider the mean values from the above mentioned methods reliable to within 10%. These mean values are

recommended for future applications and are assembled in Table II.

The comparison indicates, furthermore, that for the lighter elements the advanced theoretical methods give results as reliable as experiments. Since the former involve less time and effort (the Coulomb approximation by Bates and Damgaard is generally available), they should be extensively applied. On the other hand, experimental determination of transition probabilities should be concentrated on transitions where interferences in the transition integrals or deviations from LS coupling occur.

Application of a Kinetic Model to Time-Dependent Density Correlations in Fluids*

SIDNEY YIP AND MARK NELKIN

Department of Engineering Physics and Materials Science, Cornell University, Ithaca, New York

(Received 8 April 1964)

The kinetic model of Bhatnagar, Gross, and Krook is used to study the double Fourier transform of the time-dependent density correlation function $G(r,t)$. The results are appropriate to a dilute fluid for arbitrary ratio of wavelength to mean free path. The results of the model calculations are compared to those derived from the linearized hydrodynamic equations. Since neutron and light-scattering experiments can be analyzed in terms of $G(r,t)$, this comparison indicates that the hydrodynamic description should be applicable for momentum transfers less than $(\hbar/2\lambda)$, where λ is the collision mean free path in the fluid.

I. INTRODUCTION

THE theory of nonequilibrium phenomena has been significantly extended by the development of relationships between the linear response of a system to an external disturbance and the time-dependent correlation functions expressing the propagation of equilibrium fluctuations in the system. These developments have been primarily used to give exact expressions for transport coefficients in terms of time-dependent correlation functions.¹ It is, however, sometimes profitable to use our knowledge of the linear response to determine certain properties of those correlation functions that are directly measurable.

In recent years inelastic scattering of slow neutrons has become an important process for the study of molecular dynamics in condensed states of matter.² In a well-known work Van Hove³ showed that the energy and angle differential cross section is proportional to the double Fourier transform of a time-dependent correlation function $G(\mathbf{r},t)$. By definition, $G(\mathbf{r},t)$ is the equilibrium ensemble average of a product of two time-dependent density operators and is therefore

closely related to the linear response of the system to an externally induced density disturbance. As recently emphasized by Kadanoff and Martin,⁴ connections of this type can be usefully exploited, particularly in the limit of slow space and time variation. In the present work we consider arbitrarily fast space and time variation, but are restricted to the limit of low density.

Since $G(\mathbf{r},t)$ is in general complex its interpretation as a time-displaced, density-density correlation function has no simple physical meaning.⁵ On the other hand, the physical content of this function is simply revealed when it is considered in classical terms. For then $G(\mathbf{r},t)$ gives the probability per unit volume of finding an atom at (\mathbf{r},t) given an atom at the origin at $t=0$ and clearly describes the space-time evolution of density correlations in the system. In the following sections we make explicit use of this physical interpretation; consequently, the calculation concerns only classical systems.⁶

When a system initially in equilibrium is perturbed very slightly, its behavior, except for short-time transients, can be described in terms of the variations of a small number of macroscopic quantities. Moreover,

* Work supported in part by the U. S. Atomic Energy Commission.

¹ R. Kubo, *Lectures in Theoretical Physics* (Interscience Publishers, Inc., New York, 1959), Vol. I, Chap. 4.

² *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1961); also Vol. I, 1963.

³ L. Van Hove, *Phys. Rev.* **95**, 249 (1954).

⁴ L. Kadanoff and P. C. Martin, *Ann. Phys. (N. Y.)* **24**, 419 (1963).

⁵ For an interpretation of the imaginary part of $G(\mathbf{r},t)$, see L. Van Hove, *Physica* **24**, 404 (1958).

⁶ The relation between neutron scattering and the classical correlation function has been studied by R. Aamodt, K. M. Case, M. Rosenbaum, and P. F. Zweifel, *Phys. Rev.* **126**, 1165 (1962).

with the system in local thermodynamic equilibrium, the ensuing changes will occur only gradually. Since the linear response of the system in these situations can be calculated on the basis of linearized hydrodynamic equations, the same equations can therefore be used to determine the long-wavelength components of the corresponding time-dependent correlation functions. It is widely recognized that the density correlation function $G(\mathbf{r}, t)$ has a hydrodynamic limit for slowly varying disturbances.^{3,7} This limit exists for any fluid, and in neutron scattering it is a general result to be expected at sufficiently small momentum transfer.

The two processes which characterize hydrodynamical behavior of a classical one-component fluid are sound propagation and heat conduction. The importance of the latter in connection with scattering near the critical temperature has been examined by Van Hove.³ The presence of sound-wave propagation gives rise to a peak in the inelastic portion of the scattered neutron spectrum. This sound-wave peak is a quite general feature of an interacting many-body system. For liquid helium II near absolute zero,⁸ or for a harmonically vibrating crystal lattice, it can be described as the emission and absorption of single, freely propagating phonons. For helium at higher temperature or for a classical fluid, it can be described in terms of a more conventional local thermodynamic equilibrium disturbance which is propagated by frequent collisions. Recently, Egelstaff⁹ and Ruijgrok¹⁰ have considered the excitation of sound waves as a basic process in coherent neutron scattering by simple classical liquids. It is interesting that they reached similar conclusions, although Ruijgrok started from approximate hydrodynamic equations while Egelstaff started by analogy to a polycrystalline solid. Perhaps the most interesting application of the linearized hydrodynamic equations is to liquid helium II, where heat conduction is replaced by second-sound propagation. The possibility of seeing a second-sound peak in neutron scattering has been recently discussed by Hohenberg and Martin.¹¹

The hydrodynamic limit is not sufficient to determine the behavior of $G(\mathbf{r}, t)$ in the space-time region of interest for neutron-scattering experiments. A theory at the molecular level is needed, but a calculation from first principles for a liquid is not feasible. There have been several attempts to develop a theory of neutron scattering in liquids in terms of specific dynamical models.^{12,13} These theories have been primarily focused on the self-correlation function $G_s(\mathbf{r}, t)$, which gives the probability per unit volume of finding an atom at

position \mathbf{r} and time t knowing that the *same* atom was at the origin at time zero. The motion of a single atom described by $G_s(\mathbf{r}, t)$ is then related to $G(\mathbf{r}, t)$ through Vineyard's¹² convolution approximation. This approximation is known to fail in the hydrodynamic limit¹⁴ appropriate to small-momentum transfer, but its applicability in the range of momentum transfer currently accessible to experiment is an unresolved question.

We would like to have a molecular theory which demonstrably has the correct hydrodynamic limit. Even if this can be done only for a highly idealized system, we will then have some idea as to the range of applicability of the hydrodynamic equations in calculating the density correlation function. Since the linearized hydrodynamic equations give explicit expressions for the scattered neutron energy distribution in terms of thermodynamic derivatives and transport coefficients,⁴ an indication of their range of applicability would be quite useful. The only system for which we have such a theory is the dilute gas. As long as we restrict our attention to a time scale long compared to the duration of a collision, the response to a small density disturbance in a gas can be calculated from the Boltzmann equation.¹⁵ In particular, the linearized Boltzmann equation provides an appropriate description of sound propagation in gases¹⁶ for arbitrary frequency.

In this paper we consider a description of $G(\mathbf{r}, t)$ based on the linearized Boltzmann equation. By specifying an appropriate initial condition the integral of the phase-space distribution over velocity can be identified with $G(\mathbf{r}, t)$. Actually, the description can be made appropriate for either $G(\mathbf{r}, t)$ or $G_s(\mathbf{r}, t)$, depending on the particular form of the equation employed. This was recently pointed out by Nelkin and Ghatak¹⁷ in using the linearized Boltzmann equation of neutron transport theory (in which the collisions do not conserve energy and momentum) to calculate $G_s(\mathbf{r}, t)$. In order to simplify the computation these authors introduced an approximate transition probability. A similar approach is followed here, but since $G(\mathbf{r}, t)$ corresponds to the evolution of a density disturbance it is essential that our approximation does not distort the basic propagation mechanisms by violating the kinematical laws of conservation. In fact, the conservation of energy and momentum constitutes the only difference between our description of $G(\mathbf{r}, t)$ and that of $G_s(\mathbf{r}, t)$ in Ref. 17, but this difference makes the calculations considerably more complicated.

The kinetic model which we employ is already in use in other contexts related to rarefied gas dynamics. In the next section we discuss briefly the model and pro-

⁷ P. G. deGennes, *Physica* **25**, 825 (1959).

⁸ Michael Cohen and Richard P. Feynman, *Phys. Rev.* **107**, 13 (1957).

⁹ See P. Egelstaff in Ref. 2 (1963), Vol. I, p. 203.

¹⁰ Th. W. Ruijgrok, *Physica* **29**, 617 (1963).

¹¹ P. C. Hohenberg and P. C. Martin, *Phys. Rev. Letters* **12**, 69 (1964).

¹² G. H. Vineyard, *Phys. Rev.* **110**, 999 (1958).

¹³ K. S. Singwi and A. Sjölander, *Phys. Rev.* **119**, 863 (1960); A. Rahman, K. S. Singwi, and A. Sjölander, *ibid.* **126**, 997 (1962).

¹⁴ P. G. deGennes in Ref. 2 (1961), p. 239.

¹⁵ H. Grad, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1958), Vol. 12, p. 205.

¹⁶ G. E. Uhlenbeck and G. W. Ford, *Lectures in Statistical Mechanics* (American Mathematical Society, Providence, Rhode Island, 1963).

¹⁷ Mark Nelkin and Ajoy Ghatak, *Phys. Rev.* **135**, A4 (1964).

ceed to identify $G(\mathbf{r},t)$ with the solution of the transport equation. In our context the model enables us to evaluate the Fourier transform of $G(\mathbf{r},t)$ exactly in terms of analytic functions. This evaluation is somewhat simpler if we relax the requirement of energy conservation. The calculation is applicable to arbitrary ratio of wavelength of the disturbance to mean free path; in particular, the correct hydrodynamic limit is obtained. In Sec. III we discuss the comparison of our results with those based on the linearized hydrodynamic equations and examine the applicability of the latter in the region where the wavelength is comparable to the mean free path.

II. DESCRIPTION OF $G(\mathbf{r},t)$

In formulating a description of $G(\mathbf{r},t)$ we are interested in the response of a molecular system to a microscopic density disturbance. It is clear from the physical interpretation of the correlation function that this disturbance arises as a result of the localization of a particle. Because the system deviates from equilibrium very slightly the space-time evolution of the disturbance can be appropriately described by the linearized Boltzmann equation with proper initial condition. The problem is well defined once the connection between $G(\mathbf{r},t)$ and the solution of the linear transport equation is established. The task of actually solving the Boltzmann equation for a particular two-body interaction is sufficiently involved that, in an initial attempt, we consider the alternative approach of using a kinetic model as an approximate description.

In simplifying the transport equation, we replace the detailed description of the interatomic collisions by a single parameter model. As long as this model is constructed to maintain the conservation of particle number, momentum, and energy, the essential features of the propagation of a density disturbance will be correctly described. The kinetic equation that we use is

$$\left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla\right) f(\mathbf{r}, \mathbf{v}, t) = \alpha \left\{ F(v) Z(\mathbf{r}, t) - f(\mathbf{r}, \mathbf{v}, t) + \rho F(v) \left[\frac{2}{v_0^2} \mathbf{v} \cdot \mathbf{q}(\mathbf{r}, t) + \left(\frac{v^2}{v_0^2} - \frac{3}{2} \right) \frac{\tau(\mathbf{r}, t)}{T_0} \right] \right\}, \quad (1)$$

where f is the deviation from equilibrium of the one-particle distribution function, $n(\mathbf{r}, \mathbf{v}, t) = \rho F(v) + f(\mathbf{r}, \mathbf{v}, t)$, and ρ is the constant density. Other symbols are defined as follows:

$$\begin{aligned} F(v) &= (\pi v_0^2)^{-3/2} \exp(-v^2/v_0^2), \\ v_0^2 &= \frac{2kT_0}{M}, \\ \mathbf{q}(\mathbf{r}, t) &= (1/\rho) \int d^3v \mathbf{v} f(\mathbf{r}, \mathbf{v}, t), \\ Z(\mathbf{r}, t) &= \int d^3v f(\mathbf{r}, \mathbf{v}, t), \\ \rho T_0^{-1} \tau(\mathbf{r}, t) &= (1/3v_0^2) \int d^3v v^2 f(\mathbf{r}, \mathbf{v}, t) - Z(\mathbf{r}, t), \end{aligned} \quad (2)$$

where M is the atomic mass, T_0 is the equilibrium temperature of the fluid, and τ is the deviation in the local temperature, $T = T_0 + \tau$. The quantity α is a constant and is the parameter of this model. Equation (1) is the linearized form of a model first proposed by Bhatnagar, Gross, and Krook¹⁸ (BGK); subsequently it has been used in a variety of applications.^{19,20} One can readily verify that all the collisional invariants are preserved and that an H theorem exists. The connection between this equation and the linearized Boltzmann equation has been demonstrated by Gross and Jackson.^{20,21} They showed that (1) follows immediately from the Boltzmann equation if all the nonzero eigenvalues of the collision operator are approximated by a single constant α . This parameter has the interpretation of a relaxation frequency so the BGK model is often called the single-relaxation-time model. Since the zero eigenvalues are a consequence of conservation laws one can expect the kinetic model to give reasonable results for macroscopic quantities, particularly in the hydrodynamic region. Considerations of the stress tensor and heat flux as far as the second (Burnett) approximation indicate that this is indeed the case.²² In the same spirit one can employ more elaborate models characterized by a number of relaxation times.²³ A description with more adjustable parameters allows more latitude in the scope of application, but it also loses much of the simplicity which is the essential advantage of a kinetic model.

To study $G(\mathbf{r},t)$ we consider the initial value problem with

$$f(\mathbf{r}, \mathbf{v}, 0) = F(v) \delta(\mathbf{r}). \quad (3)$$

It is necessary that the particle initially localized at the origin have a Maxwellian distribution in velocity because inherent in the definition of the correlation function is an ensemble average. We now make the identification

$$G(\mathbf{r}, t) = Z(\mathbf{r}, t) + \rho \quad (4)$$

since the two quantities have the same physical interpretations. Equations (1) through (4) therefore constitute our description of $G(\mathbf{r},t)$.

In their original application of the kinetic model BGK considered the problem of small-amplitude oscillations in gases. This is the same problem envisaged here. Their calculations, however, need to be extended for our purposes since they studied in detail only the dispersion relation and we require explicitly the velocity integral of the distribution function. Actually, the corre-

¹⁸ P. F. Bhatnagar, E. P. Gross, and M. Krook, *Phys. Rev.* **94**, 511 (1954).

¹⁹ For example, E. P. Gross and M. Krook, *Phys. Rev.* **102**, 593 (1956); E. P. Gross, E. A. Jackson, and S. Ziering, *Ann. Phys. (N. Y.)*, **1**, 141 (1957).

²⁰ E. P. Gross and E. A. Jackson, *Phys. Fluids* **2**, 432 (1959).
²¹ E. P. Gross, in *Rarefied Gas Dynamics*, edited by F. M. Devienne (Pergamon Press, Ltd., London, 1960), p. 139.

²² H. T. Yang, *Phys. Fluids* **2**, 237 (1959).
²³ L. Sirovich and J. K. Thurber, in *Rarefied Gas Dynamics*, edited by J. A. Laurman (Academic Press Inc., New York, 1963), Vol. I, p. 159.

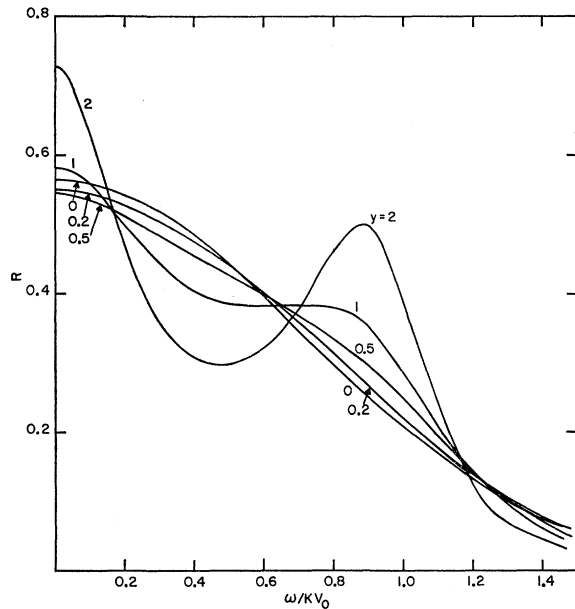


FIG. 1. System response to a microscopic density disturbance for various ratios (ratio = $2\pi\sqrt{2}y$) of wavelength to mean free path as calculated from Eqs. (6) and (7), $R = (Kv_0/\pi)S(x, y)$.

lation function $G(\mathbf{r}, t)$ is not a quantity of direct experimental interest. What is measured in neutron scattering is its Fourier transform

$$\begin{aligned} S(\mathbf{K}, \omega) &= \int_{-\infty}^{\infty} dt \int d^3r G(\mathbf{r}, t) e^{i(\mathbf{K} \cdot \mathbf{r} - \omega t)} \\ &= 2 \operatorname{Re} \int_0^{\infty} dt \int d^3r G(\mathbf{r}, t) e^{i(\mathbf{K} \cdot \mathbf{r} - \omega t)}. \end{aligned} \quad (5)$$

The second relation holds because $G(\mathbf{r}, t)$ is even in t . For isotropic systems $G(\mathbf{r}, t)$ is a function only of the magnitude of \mathbf{r} , so S which is even in ω depends only on the magnitude of \mathbf{K} .

In scattering problems the variables $\hbar K$ and $\hbar\omega$ represent momentum and energy transfers, but with regard to the kinetic equation K and ω are more appropriately interpreted as the wave number and angular frequency of the density disturbance. This is an explicit manifestation of the relation between equilibrium density fluctuations and the neutron-scattering properties of the system.

The calculation of $S(\mathbf{K}, \omega)$ is a straightforward matter and the reader is referred to BGK for details of the solution of Eq. (1). After a number of algebraic manipulations we obtain

$$S(x, y) = \frac{2}{Kv_0} \left(\frac{\gamma_1 \gamma_3 + \gamma_2 \gamma_4}{\gamma_3^2 + \gamma_4^2} \right), \quad (6)$$

where we have introduced the dimensionless variables

$$x = -\omega/Kv_0 \quad \text{and} \quad y = \alpha/Kv_0,$$

and the γ_n are defined by

$$\begin{aligned} \gamma_1 &= a_5 B_1 - a_6 B_2 + y(a_3 C_1 - a_4 C_2), \\ \gamma_2 &= a_6 B_1 + a_5 B_2 + y(a_4 C_1 + a_3 C_2), \\ \gamma_3 &= a_1 B_1 - a_2 B_2 + y(a_3 A_1 - a_4 A_2), \\ \gamma_4 &= a_2 B_1 + a_1 B_2 + y(a_4 A_1 + a_3 A_2), \end{aligned} \quad (7)$$

with

$$\begin{aligned} a_1 &= 1 - yU - 2xy\epsilon_1, & a_2 &= -y(V + 2x\epsilon_2), \\ a_3 &= \epsilon_3 - U/2, & a_4 &= \epsilon_4 - V/2, \\ a_5 &= U/2 + y\epsilon_2, & a_6 &= V/2 - y\epsilon_1, \\ \epsilon_1 &= xU - yV, & \epsilon_2 &= xV + yU - 1, \\ \epsilon_3 &= (x^2 - y^2)U - 2xyV + y, & \epsilon_4 &= (x^2 - y^2)V + 2xyU - x, \\ A_1 &= 1 - \frac{2}{3}y(\epsilon_3 + x\beta_1 + U + 2x\epsilon_1), \\ A_2 &= -\frac{2}{3}y(\epsilon_4 + x\beta_2 + V + 2x\epsilon_2), \\ B_1 &= 1 - \frac{1}{3}y(\epsilon_3 + x\beta_1 + U - y\beta_2), \\ B_2 &= -\frac{1}{3}y(\epsilon_4 + x\beta_2 + V + y\beta_1), \\ C_1 &= \frac{1}{3}(\epsilon_3 + y\beta_2 + U + 2y\epsilon_2), \\ C_2 &= \frac{1}{3}(\epsilon_4 - y\beta_1 + V - 2y\epsilon_1), \\ \beta_1 &= 2(x^2 - y^2)(xU - yV) + 4xy(1 - yU - xV), \\ \beta_2 &= 2(x^2 - y^2)(xV + yU - 1) + 4xy(xU - yV) - 1, \\ U &= (\pi)^{1/2} U'(x, y), & V &= (\pi)^{1/2} V'(x, y). \end{aligned}$$

The functions U' and V' are, respectively, the real and imaginary parts of the probability integral of complex argument,

$$\begin{aligned} W(x + iy) &= U'(x, y) + iV'(x, y) \\ &= \frac{i}{\pi} \int_{-\infty}^{\infty} dt \frac{e^{-t^2}}{x - t + iy}. \end{aligned} \quad (8)$$

Using tabulated values of U' and V' ²⁴ we have computed S as a function of x for different values of y . Some typical results are plotted in Fig. 1 in terms of the dimensionless quantity $R = (Kv_0/\pi)S$. For comparison we show in Fig. 2 corresponding results calculated in the isothermal approximation¹⁸ ($\tau = 0$). This approximation simplifies the algebra considerably, and we find that S in this case is also given by (6) but (7) is replaced by

$$\begin{aligned} \gamma_1 &= U(y^2 + \frac{1}{2}) + xyV - y, \\ \gamma_2 &= V(y^2 + \frac{1}{2}) - xyU, \\ \gamma_3 &= 1 - yU(1 + 2x^2) + 2xy^2V, \\ \gamma_4 &= 2xy - yV(1 + 2x^2) - 2xy^2U. \end{aligned} \quad (9)$$

As we examine the results in Figs. 1 and 2, we see that all the general features of density correlation are displayed in the Fourier components of $G(\mathbf{r}, t)$. In these

²⁴ V. N. Faddeyeva and N. M. Terent'ev, *Tables of the Probability Integral for Complex Arguments* (Pergamon Press, Ltd., London, 1961).

calculations the dimensionless parameter y is a measure of the wavelength of the disturbance as compared to the collision mean free path. Thus, the Knudsen region is characterized by $y \ll 1$, whereas the hydrodynamic region corresponds to $y \gg 1$. When collisions are rare (small y) all disturbances dissipate by free particle flow, and since these motions are uncorrelated the higher frequency components are more strongly attenuated. In the collisionless limit we have

$$\lim_{y \rightarrow 0} S(x, y) = [(\pi)^{1/2} K v_0]^{-1} \exp(-x^2). \quad (10)$$

This is a general result independent of models. It is easily checked analytically that the isothermal calculation gives this limit correctly, and the numerical results using (7) also satisfy (10). As the wavelength becomes comparable to the mean free path, correlation effects from successive collisions become appreciable and thereby cause the attenuation at certain frequencies to be markedly reduced. For very long wavelength disturbances the response varies sharply with frequency. This is the region where transport processes are dominated by collisions so it is not surprising that the isothermal approximation gives significantly different results.

The present calculations for large y are particularly simple to interpret in terms of equilibrium density fluctuations. The processes involved arise as a consequence of fluctuations in pressure and temperature (or entropy). The mechanical and thermal effects are generally coupled, but at low temperatures or long wavelengths they manifest in different ways. It is well known that the pressure waves propagate adiabatically while the thermal waves diffuse.²⁵ This phenomenon, long familiar in the theory of Rayleigh scattering,²⁶ gives rise to a spectrum consisting of two equally displaced components (the Brillouin doublet) due to sound propagation and a central component due to heat conduction. The curve for $y=2$ in Fig. 1 exhibits just this behavior, while the corresponding curve in Fig. 2 shows only the sound peak, since temperature variations are ignored. It is interesting to note that the sound peak occurs in these two calculations at values of x predicted by the adiabatic and isothermal sound speeds, $(\frac{5}{6})^{1/2} v_0$ and $v_0/\sqrt{2}$, respectively. There appears to be little dispersion effect at this value of y .

Finally, it should be emphasized that by virtue of its relation to the Boltzmann equation, the kinetic model is constrained to give results appropriate to dilute fluids. This can be seen from the prediction that in the long-wavelength limit the sound-speed values are those appropriate to monatomic gases. Also, we can obtain an estimate of the ratio of specific heats as implied by the present description. It is known that the intensity ratio

²⁵ See, for example, J. Frenkel, *Kinetic Theory of Liquids*, (Oxford University Press, London, 1946).

²⁶ L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon Press, Ltd., London, 1960).

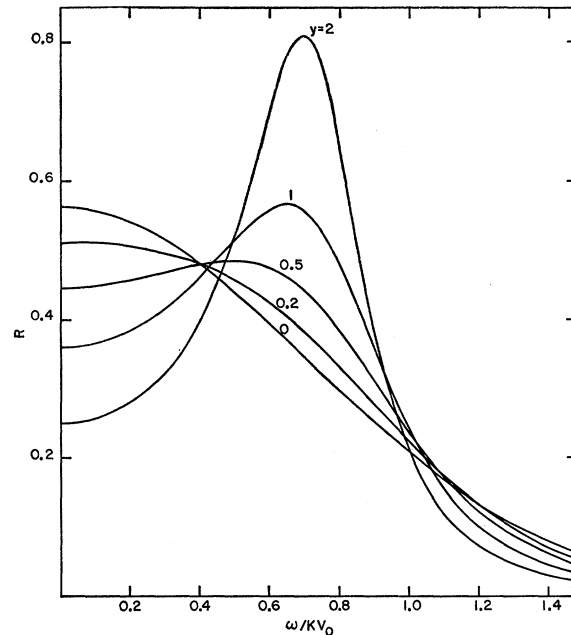


FIG. 2. Same as Fig. 1 except that the response is calculated in the isothermal approximation where S is given by Eqs. (6) and (9).

of the central peak to displaced peaks is given by $(C_p - C_v)/C_v$.²⁵ For $y=5$ we find a ratio of ~ 0.69 as compared to $\frac{2}{3}$ for ideal gases.

III. DISCUSSION

On the basis of a kinetic model in which collisions are replaced by a simple relaxation process, the energy distribution of neutrons coherently scattered by a fluid has been expressed in terms of a dimensionless parameter y . This parameter is inversely proportional to the momentum transfer and directly proportional to the relaxation frequency α , which represents the average rate at which the molecules approach local equilibrium. For large y the correct hydrodynamic limit for the density correlation function is obtained. This limit is characterized by a central peak whose width is determined by the rate of heat diffusion, and side peaks whose location and width are determined by the frequency and attenuation of sound at a given wave number K ($\hbar K$ is the momentum transfer in a scattering event). The intensity and location of the peaks are determined by thermodynamic quantities characteristic of a dilute gas, and are a consequence of the Boltzmann-like description. The widths of the peaks are determined by transport coefficients which depend on the particular kinetic model used.

The most striking qualitative feature of the present results is the presence of a sound-wave peak and its persistence in Fourier components of the density correlation function for wavelengths comparable to a mean free path. Similar structure in the inelastically scattered neutron energy distribution has often been discussed

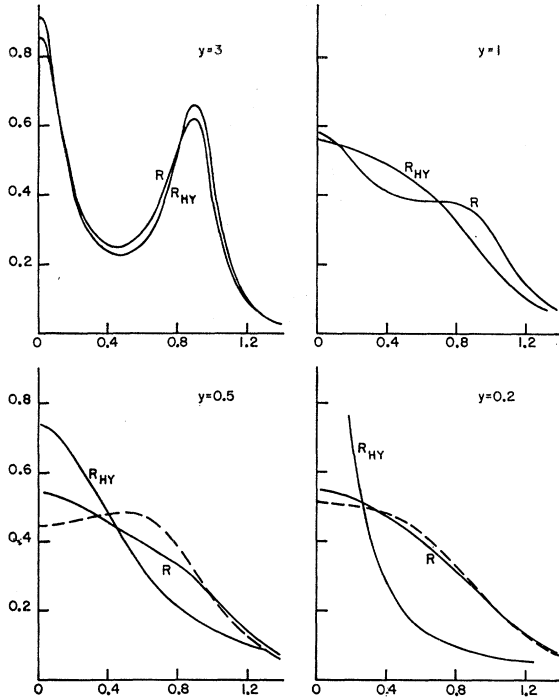


FIG. 3. Comparison of kinetic and hydrodynamic descriptions as the ratio of wavelength to mean free path decreases; R is calculated as in Fig. 1 and R_{HY} is calculated from Eq. (14). Abscissa is in units of ω/Kv_0 . Also shown are the isothermal results from Fig. 2 (dashed curves).

as an indication of solid-like behavior. The presence of such structure for a gas makes it clear that the identification of quasicrystalline atomic motions in liquids must be made with some care.

Recently, Kadanoff and Martin⁴ derived an expression for $S(K, \omega)$ from a set of linearized hydrodynamic equations appropriate to a one-component fluid. With appropriate modifications of the notation, their Eq. (87a) becomes

$$S(k, \omega) = \left(1 - \frac{C_v}{C_p}\right) \frac{D_T K^2}{\omega^2 + (D_T K^2)^2} + \frac{C_v}{C_p} \frac{c^2 K^4 \Gamma}{(\omega^2 - c^2 K^2)^2 + (\omega K^2 \Gamma)^2} \left(1 - \frac{C_v}{C_p}\right) \times \frac{D_T K^2 (\omega^2 - c^2 K^2)}{(\omega^2 - c^2 K^2)^2 + (\omega K^2 \Gamma)^2}, \quad (11)$$

where c is the sound speed, $D_T = \kappa / M\rho C_p$,

$$\Gamma = \frac{(4\eta/3 + \xi)}{M\rho} + D_T \left(\frac{C_p}{C_v} - 1\right),$$

κ is the thermal conductivity, η is the shear viscosity, and ξ is the second or bulk viscosity.

The effects of heat conduction and sound propagation

are quite clearly displayed in (11). The central peak is seen to be a Lorentzian. If the diffusivity coefficient D_T is replaced by the self-diffusion coefficient D , the central peak appropriately describes the long wavelength behavior of the self-correlation function $G_s(r, t)$. This replacement is appropriate for a gas where heat is carried entirely by particle motion but is not appropriate for a liquid. The BGK model does not allow an unambiguous calculation of the self-diffusion coefficient or of $G_s(r, t)$. Thus, even for a gas, a quantitative study of the accuracy of the convolution approximation relating $G(r, t)$ to $G_s(r, t)$ must await more accurate solutions of the appropriate linearized Boltzmann equations.

The second term in (11) describes the response to pressure disturbances and is associated with the propagation of a damped sound wave. The absorption is seen to be inversely proportional to the square of the wavelength. We expect (11) to be valid when the system is effectively in local thermodynamic equilibrium. For more rapid disturbances we expect dispersion and modified absorption. For a gas where local thermodynamic equilibrium is maintained by collisions, and structural relaxation phenomena can be ignored, we expect the BGK model to give a reasonable estimate of the range of κ for which (11) applies.

In order to compare (11) with (6), we must specialize the prediction of (11) to the BGK model. Since we start from the linearized Boltzmann equation, we are constrained to the dilute gas results

$$C_v/C_p = \frac{3}{5}, \quad c = \left(\frac{5}{6}\right)^{1/2} v_0, \quad \text{and} \quad \xi = 0. \quad (12)$$

The transport coefficients are dependent on the model. Applying the Chapman-Enskog method,¹⁶ the first approximation (Navier-Stokes) gives

$$\kappa = \frac{5}{4} \rho (k v_0^2 / \alpha) \quad \text{and} \quad \eta = \rho M v_0^2 / 2\alpha. \quad (13)$$

The same results are obtained from the nonlinear BGK model.²⁷

With these substitutions, and returning to the dimensionless variables x and y , (11) becomes

$$S(x, y) = \frac{1}{10\alpha} \left[\frac{2}{x^2 + (1/2y)^2} + \frac{5}{(x^2 - \frac{5}{6})^2 + (x/y)^2} - \frac{2(x^2 - \frac{5}{6})}{(x^2 - \frac{5}{6})^2 + (x/y)^2} \right]. \quad (14)$$

In Fig. 3 we compare the results obtained from the hydrodynamic description of Eq. (14) with those obtained from the kinetic description of Eq. (6). For $y=5$ (not shown) the curves are practically indistinguishable. For $y=3$ they are quite similar, but for $y < 1$ they become quite different. The greater persistence of the dis-

²⁷ J. L. Lebowitz, H. L. Frisch, and E. Helfand, Phys. Fluids 3, 325 (1960).

placed peak evident in the kinetic results is to be expected since the BGK model is known to predict¹⁸ a sound attenuation which increases less rapidly than the square of the frequency.

We thus find that the hydrodynamic description gives comparable results to our kinetic model for $y \gtrsim 2$. This indicates that the hydrodynamic description is reasonable for values of κ less than $(\alpha/2v_0) = (2\lambda)^{-1}$, where λ is an effective mean free path for collision.

There is no sound theoretical basis for extrapolating to moderately dense systems. In fact, it is clear that the results obtained here are not even qualitatively correct for a strongly interacting medium where appreciable local correlations exist. However, in the region where these correlation effects do not predominate, one might expect a description based upon the linearized hydrodynamic equations to be appropriate. For example, such a description should be applicable to liquids for very long wavelength disturbances. In neutron scatter-

ing, or light scattering where the process can similarly be described in terms of density correlations, this approach will break down for those momentum transfers where explicit effects of atomic structure appear in the angular distribution of the scattering. Since structure effects do not manifest in general for $\kappa \lesssim 10^8 \text{ cm}^{-1}$, Eq. (11) should provide a reasonable calculation of the scattered energy distribution at these low values of momentum transfer. This is given further plausibility by the agreement² obtained with experiments on incoherent neutron scattering on the basis of a simple diffusion model in this range of momentum transfer.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the assistance of S. Ranganathan in checking the calculations and performing the numerical computations. Use of the facilities at the Cornell University Computing Center is hereby acknowledged.

Intense 584-Å Light from a Simple Continuous Helium Plasma*

C. A. JENSEN AND W. F. LIBBY

Department of Chemistry and Institute of Geophysics, University of California, Los Angeles, California

(Received 23 March 1964)

A simple source for the production of continuous cold plasmas and intense line spectra associated with a particular gas is described in its application to helium. Plasma densities and temperatures have been measured spectroscopically. When using helium or neon gas the device becomes an intense source of ionizing radiation for studies of the chemical reactions induced by the ionizing ultraviolet. The intensity of this radiation has been measured with reasonable accuracy by very simple photocells which are easily constructed in the laboratory and are only sensitive to vacuum-ultraviolet radiator; more than 10^{16} 584-Å photons per second are emitted by a 30-W source. The mechanism is via ion-electron recombination from a 1660°K plasma of $\sim 10^{13}$ ions/cm³ density.

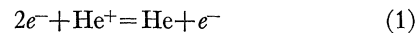
I. INTRODUCTION

THE importance of ionizing radiation in inducing chemical reactions is widely recognized. For this reason we have prepared a simple intense source of ionizing ultraviolet light, monochromatic at 584 Å, to study the chemical effects of the solar ionizing ultraviolet on planetary atmospheres and surfaces in order to contribute to the scientific base of the space program.

II. METHOD

The Sherwood project—the attempt to control thermonuclear energy—has taught us a great deal about the properties of plasmas, and in particular that for helium gas. One of the principal results is that in a moderately dense helium plasma the rate of neutraliza-

tion of He⁺ by



is very rapid.¹ In addition good methods are available for the measurement of plasma temperatures and densities.¹ With the temperatures and densities known the rate of the three-body ion-electron recombination can be calculated,^{2,3} and compared with the observed intensity of the 584-Å 2^1P-1^1S line.

Our source is a very simple and low-power device for producing plasmas of $\sim 1660^\circ\text{K}$ and number densities of 10^{13} cm^{-3} over a volume of several cubic centimeters. We find an intensity of $\sim 4 \times 10^{15}$ 584-Å photons per second cubic centimeter.

¹ E. Hinnov and J. G. Hirschberg, *Phys. Rev.* **125**, 795 (1962).

² F. Robben, W. B. Kunkel, and L. Talbot, *Phys. Rev.* **132**, 2363 (1963).

³ D. R. Bates, A. E. Kingston, and R. W. P. McWhirter, *Proc. Roy. Soc. (London)* **A267**, 297 (1962); **A270**, 155 (1962).

* This research was supported by the Directorate of Chemical Sciences, U. S. Air Force Office of Scientific Research, Grant No. AF-AFOSR 245-64.