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Failure of Bogoliubov's Functional Assumption

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In this paper we investigate the mathematical validity of Bogoliubov's functional assumption. For this purpose, we analyze a model for a system in which light particles scatter against fixed centers. We compare the exact solution for the one-body distribution function and two-body correlation function with the results given by Bogoliubov's method. We find that Bogoliubov's functional assumption is too restrictive to allow proper initialization for both functions. As a consequence, the Bogoliubov result for the two-body correlation departs drastically from the exact solution. The results obtained here are fully consistent with previous asymptotic analysis of the one- and two-body equations of the Bogoliubov-Born-Green-Kirkwood-Yvon hierarcy.

The development of nonequilibrium statistical mechanics is based largely on methods and concepts introduced by Bogoliubov.[1] The resulting theory with various modifications[2–7] has been widely accepted as the correct approach in the study of gases and stable plasmas.[8,9] Moreover, the method has been applied in a number of other areas.[10–12] It has become apparent that there are difficulties in applying Bogoliubov's method, but it has been the general belief that the failures are in the nature of technicalities rather than basic malfunctions.[13]

A higher-order theory is of critical importance for the kinetic description of a dense gas, a dense plasma, or, more generally, of a system in which three-body collisions are important. It is believed that Bogoliubov's method gives correct lowest-order results, even though attempts at a higher-order theory are not fully satisfactory. A basic feature which remains unsatisfactory in the Bogoliubov expansion to high order is the lack of a proper description of the approach to equilibrium.[14] Higher-order corrections result in an ill-defined H function so that the lowest-order Boltzmann H theorem cannot provide the needed entropy theorem for a dense system. A generally accepted interpretation of the difficulties is that three-body collisions have not been included properly in the calculations. If this is so, then indeed this would be a calculational problem which would eventually be overcome. Several attempts have been made to include three-body collisions with only limited success.[2,15,16]

Green has noted that the leading-order correlation function would be modified by three-body effects and in fact should be damped.[17] This is in contrast with the Bogoliubov theory which gives an undamped correlation. We agree with Green's suggestions, but we add that even without three-body effects a definite damping occurs. The nature of this additional damping effect, we believe is made quite clear with the aid of the solvable model discussed in this paper.

An effective alternate method for the study of transport properties is the "correlation function method."[18–20] This useful technique focuses on the transport coefficients quite directly and bypasses a detailed calculation of the velocity distribution function. It has been suggested that the correlation function method [J. R. Dorfman (private communication)] eliminates the difficulties that occur when Bogoliubov's method is used. However, a method that bypasses a description of the kinetic level is incomplete and does not shed light directly on the failings of the Bogoliubov method.

In recent work, we have shown by explicit calculation of the two-particle correlation function that the difficulties in the Bogoliubov method are of a fundamental nature and not, as originally presumed, a technical problem.[21–24] In a recent paper, Pomeau confirms our results with a different calculational method.[25] As a consequence, the two-body correlation function given by Bogoliubov's expansion is miscalculated in a definite region of phase space even in lowest order. The purpose of this paper is to determine the detailed mechanism of the previously demonstrated failure of Bogoliubov's method. Toward this end we have constructed and studied an exactly solvable model. For the proposed model described below, we analyze in detail a properly set initial boundary-value problem and compare the exact solution with Bogoliubov's results. In Appendix A, the motivation of our model is discussed by studying the relationship between the equations of the "Lorentz" gas and those of the model. The model is designed to understand the approximation methods that are used to solve the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy and not designed to give estimates of relaxation times or transport coefficients. The model equations are formally similar (Appendix A) to the equations of nonequilibrium statistical mechanics that govern the evolution of the one-body distribution function and the two-body correlation function. Because of this similarity, it is convenient to retain the language appropriate for a Lorentz gas in the description of the model and of its solution. Thus, in our discussion, we refer to a system in which light particles are scattered by fixed centers. It should be emphasized though that we are working with a model and that the main objective of this paper is to check the mathematical applicability of Bogoliubov's approximation technique.

We consider the equations

$$\frac{\partial f}{\partial t} = -\epsilon \int d\vec{x}\, I(\vec{x}) g(\vec{x}, t) , \tag{1}$$

$$\frac{\partial g}{\partial t} + \vec{v} \cdot \vec{\nabla} g = I(\vec{x}) f(t) , \tag{2}$$

where f corresponds to the nonequilibrium part of the one-body velocity distribution function and g to the nonequilibrium part of the two-body correlation function [see Appendix A, Eqs. (A8) and (A9)]. We interpret $\vec{x}$ and $\vec{v}$ as the position and velocity vectors of the light particle and I as an interaction function generated by a fixed scattering center at the origin. We consider the nonequilibrium evolution of the gas as an initial boundary-value problem. The system has settled over a sufficiently long period of time to thermodynamic equilibrium. At $t=0$ the velocity distribution is disturbed without changing the two-body correlation from its equilibrium value. The subsequent evolution of the system is then studied.

We have obtained solutions for f and g, employing a number of interaction functions, and found that the basic features of the results are independent of the nature of $I(\vec{x})$. In particular, we have studied Debye, square-barrier, and δ-function interactions. The analysis is most transparent with the choice of the δ-function interaction and with a system in which motion is restricted to one dimension. As indicated in Appendix A, our choice of δ-function interaction is motivated by the fact that a square-barrier potential results in a δ-function force. For the δ-function interaction, Eqs. (1) and (2) reduce to

$$\frac{df}{dt} = -\epsilon \int_{-\infty}^{+\infty} dx\, \delta(x-\alpha) g(x, t) , \tag{3}$$

$$\frac{\partial g}{\partial t} + \frac{\partial g}{\partial x} = \delta(x) f(t) , \tag{4}$$

where α is a small positive constant introduced for mathematical rigor which can be set equal to zero at the end of the calculation. In our one-dimensional form of the equations for f and g, x is the component of relative separation parallel to the relative velocity, which for simplicity we set equal to $+1$ so that the light particle moves to the right with unit speed. We emphasize that an ensemble of systems is considered. Each representative of the ensemble can be thought of as a large box containing a single heavy and a single light particle. Since we neglect three-body interactions, only a single collision contributes to the correlation. The location x of the light particle at time t is related to its location x_0 at the time $t=0$ (i.e., when the gas is disturbed) by

$$x = x_0 + t . \tag{5}$$

Since the location of the heavy particle is taken at the origin, the position of the light particle, x, is negative before collision and positive after collision.

The exact solutions for the nonequilibrium velocity distribution function and correlation function (with suitable normalization), in the limit $\alpha \to 0$, are

$$f(t) = e^{-\epsilon t} , \tag{6}$$

$$g(x, t) = \Theta(x)\Theta(t-x)\Theta(t) e^{-\epsilon(t-x)} , \tag{7}$$

where Θ is the Heaviside step function defined by

$$\Theta(x) = \begin{cases} 1, & x > 0 \\ 0, & x < 0 \end{cases} . \tag{8}$$

The solution for g as given by Eq. (7) is plotted in Fig. 1 as a function of x for a particular value of t.[26] Since the heavy particle is stationary, the position of the light particle (i.e., x) represents at time t the separation of the interacting particles. Note that although we refer to a single light particle, this particle is representative of an ensemble. The behavior of the correlation is interpreted as follows.

$x > t$: At the time of the disturbance, the light particle is to the right of the heavy particle. From Eq. (5), it follows that $x_0 > 0$ so that the collision occurred before the gas was disturbed. Collisions that occurred when the system was in equilibrium do not contribute to the nonequilibrium correlation.

$x = t$: The collision occurs at the time the system is disturbed (i.e., $x_0 = 0$). These collisions provide the maximum contribution to the nonequilibrium correlation.

$0 < x < t$: This range of x corresponds to light

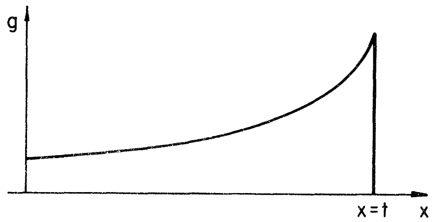

FIG. 1. Exact correlation as a function of x for a given time t.

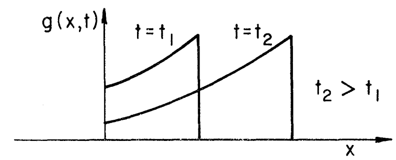

FIG. 2. Evolution of the two-body correlation as a function of x with time as a parameter.

particles that are initially located between $x_0 = -t$ and $x_0 = 0$. It is reasonable that the longer the delay between the disturbance from equilibrium and the occurrence of the collision, the smaller the contribution is to the nonequilibrium correlation. This is because the system has partially relaxed to equilibrium.

$x < 0$: The collision will occur at a time greater than t so that light particles with $x < 0$ make no contribution to the nonequilibrium correlation at time t.

The exact $g(x, t)$ is plotted as a function of x with t as a parameter in Fig. 2. Since $g(x, t) = 0$ for $t < 0$, there is no contribution to the nonequilibrium correlation prior to the time that the system is disturbed. The location of the peak value of g is the position at time t of that light particle which collided with the heavy one at $t = 0$, i.e., at the instant the gas was disturbed. Thus, in Fig. 2, we see that the correlation function has a wavelike propagation.

The exact solution for g described above will now be compared with the result for g that is obtained using Bogoliubov's adiabatic assumption; namely, g depends on time only through f. In Appendix B, we outline the procedure for deriving the Bogoliubov series. The result of summing the entire Bogoliubov series yields as $\alpha \to 0$

$$f_B = e^{-\epsilon t} , \tag{9}$$

$$g_B = \sum_{n=0}^{\infty} \epsilon^n g_B^{(n)} = \Theta(x) e^{-\epsilon t} e^{+\epsilon x} . \tag{10}$$

Equation (10) shows that Bogoliubov's method gives a correlation that *diverges* exponentially with increasing separation of the light and heavy particles. Particles that collided long before the system is disturbed from equilibrium yield exponentially large contributions to the nonequilibrium correlation. This is unacceptable since collisions that occurred when the system was in equilibrium cannot contribute to the nonequilibrium correlation. Thus, Bogoliubov's result for the correlation function is nonphysical.

In kinetic-theory analysis we can only compute the first few terms of Bogoliubov's series given in Eq. (10). We thus examine the leading-order Bogoliubov approximation. This results in a velocity distribution function given by

$$f_B = e^{-\epsilon t} \tag{11}$$

and a correlation function given by

$$g_B^{(0)}(x, t) = \Theta(x)\Theta(t)e^{-\epsilon t} . \tag{12}$$

The leading Bogoliubov result in Eq. (12) indicates that at a given time particles which collided long before, immediately after, and long after the system was disturbed provide the same contribution to the nonequilibrium correlation. The higher-order terms in Bogoliubov's series, rather than improving the situation, make it worse. The results are compared in Fig. 3.

Note that Bogoliubov's result is approximately correct for small particle separation and fails for large separation. It is this important characteristic of Bogoliubov's result which allowed him to obtain a proper leading-order kinetic equation for stable systems. Since the interaction potential vanishes for large particle separation, the incorrect features of the correlation function (as calculated by Bogoliubov) do not contribute to the collision integral. The miscalculated lowest-order correlation, however, seriously affects initially unstable systems as well as higher-order kinetic corrections.

In this paper, we have shown that the coupled equations for f and g [Eqs. (3) and (4)] have well-defined and meaningful solutions, provided that at

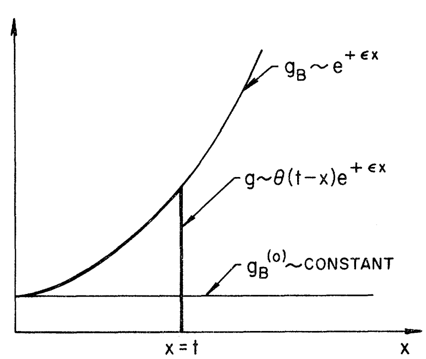

FIG. 3. Comparison of the exact correlation function with the results of Bogoliubov's method. The area under $g(x,t)$ as a function of x is finite for all t while the corresponding area diverges for the Bogoliubov results.

$t=0$ both f and g are specified independently. In contrast, the functional assumption does not allow sufficient freedom to properly initialize both f and g. Thus, the solution obtained for g based on Bogoliubov's assumption is very restricted. It is not unreasonable, therefore, that Bogoliubov's solution does not describe a physically realizable system. In fact, from inspection of Eq. (12), we see that Bogoliubov's correlation at $t=0^+$ grows exponentially with separation, implying that interactions which occur prior to the disturbance of the system contribute to the nonequilibrium correlation. Even worse, the contribution is larger the earlier the interaction occurs.

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APPENDIX A: MOTIVATION OF THE MODEL EQUATIONS

A Lorentz gas is constituted by stationary centers that scatter light particles which do not interact among themselves. The stationary centers can be associated with massive particles. The equations of the BBGKY hierarchy for the Lorentz gas can be written

$$\frac{\partial F^s}{\partial t}+\vec{v}\cdot\vec{\nabla}F^s=\frac{\phi_0}{kT}I^sF^s+(nr_0^3)\frac{\phi_0}{kT}\int d\vec{x}_{s+1}I_{s+1}F^{s+1}, \tag{A1}$$

where the interaction operators are given by

$$I_i=I_i(\vec{x}-\vec{x}_i)=\frac{\partial\phi}{\partial\vec{x}}(\vec{x}-\vec{x}_i)\cdot\frac{\partial}{\partial\vec{v}}, \tag{A2}$$

$$I_s=\sum_{i=1}^{s-1}I_i=\sum_{i=1}^{s-1}\frac{\partial\phi}{\partial\vec{x}}(\vec{x}-\vec{x}_i)\cdot\frac{\partial}{\partial\vec{v}} \tag{A3}$$

The function F^s is the distribution for one light particle and $(s-1)$ heavy particles. We assume that we have a weakly coupled gas so that the potential energy is small compared to the kinetic energy and that the number of particles within the range of interaction of a given center is neither very small nor very large; i.e.,

$$\frac{\phi_0}{kT}\ll 1,\quad nr_0^3\sim 1. \tag{A4}$$

We consider a spatially homogeneous gas which implies that the one-body distribution function is independent of position and that the two-body distribution function depends only on the relative position of the light and heavy particles. We introduce the two-body correlation G by

$$F^2=F^1+\epsilon G, \tag{A5}$$

so that when $s=1$ and $s=2$, Eq. (A1) reduces to

$$\frac{\partial F^1}{\partial t}=\epsilon\int d\vec{x}\,\frac{\partial\phi}{\partial\vec{x}}\cdot\frac{\partial G}{\partial\vec{v}}, \tag{A6}$$

$$\frac{\partial G}{\partial t}+\vec{v}\cdot\vec{\nabla}G=\frac{\partial\phi}{\partial\vec{x}}\cdot\frac{\partial F^1}{\partial\vec{v}}+O(\epsilon). \tag{A7}$$

The terms neglected on the right-hand side of Eq. (A7) include three-body effects.

The equations for the Lorentz gas, Eqs. (A6) and (A7), are linear. Therefore, we introduce the decomposition of both the distribution and correlation functions into equilibrium and nonequilibrium components:

$$F^1=F^1_{\text{eq}}+f, \tag{A8}$$

$$G=G_{\text{eq}}+g. \tag{A9}$$

The equations for the nonequilibrium components are

$$\frac{\partial f}{\partial t}=\epsilon\int d\vec{x}\,Ig(x,t), \tag{A10}$$

$$\frac{\partial g}{\partial t}+\vec{v}\cdot\vec{\nabla}g=If. \tag{A11}$$

We have studied the one-dimensional model equations for f and g,

$$\frac{\partial f}{\partial t}=-\epsilon\int dx\,Ig(x,t), \tag{A12}$$

$$\frac{\partial g}{\partial t}+v\frac{\partial g}{\partial x}=I(x)f, \tag{A13}$$

where $I(x)$ is no longer an operator but a function. The choice for the sign of ϵ in the model equation for f [Eq. (A12)] is opposite to that which appears in Eq. (A10). This change is motivated by the following stability considerations. The integrodifferential equation for f in the Lorentz gas is

$$\frac{\partial f}{\partial t}=+\epsilon\int_0^t d\lambda\left(\frac{\partial}{\partial\vec{v}}\,\underline{\underline{T}}\,\frac{\partial}{\partial\vec{v}}\right)f(t-\lambda), \tag{A14}$$

where

$$T_{ij}=\int\frac{\partial\phi}{\partial x_i}\,\frac{\partial\phi(\vec{x}-\vec{v}\lambda)}{\partial x_j}\,d\vec{x}. \tag{A15}$$

For times on the kinetic scale, we have

$$\frac{\partial}{\partial v_i}\int_0^\infty d\lambda\,T_{ij}\frac{\partial}{\partial v_j}<0. \tag{A16}$$

It is this condition that results in stability for F. However, when the operator I is replaced by a δ function, the above inequality is reversed and stability is reestablished by reversing the sign of ϵ. It should also be noted that when three-body collisions are neglected, the collisional integral vanishes for the one-dimensional Lorentz gas. However, for the model this is not the case, so we can obtain the general features of the model functions f and g subject to the approximation of no three-body collisions without resorting to three-dimensional analysis.

Finally, we observe that in the one-dimensional situation, if we investigate a square-hat potential, namely,

$$\phi(x) = \begin{cases} 1, & |x| < a \\ 0, & |x| > a \end{cases} \tag{A17}$$

we obtain an interaction function

$$I \propto \frac{\partial \phi}{\partial x} = \delta(x+a) - \delta(x-a) \; . \tag{A18}$$

Thus, it is the square-well potential that has motivated our choice of $I = \delta(x)$. It can be shown with the I given in (A18) that stability is maintained automatically without reversing the sign of ϵ.

APPENDIX B: RESULTS BASED ON BOGOLIUBOV'S TECHNIQUE

Bogoliubov has given a completely systematic expansion method for the equations of nonequilibrium statistical mechanics. The basis of his method is given in Eqs. (B1), (B3), and (B8) below. These unambiguously select a solution of the equations for f and g.

The leading-order Bogoliubov results for f and g are given in Eqs. (11) and (12) and the resummed results are given in Eqs. (9) and (10). We demonstrate below that these results follow from the application of Bogoliubov's functional assumption which states that g depends upon time only through the dependence of f on time; i.e.,

$$g_B(x, \; t) = g_B(x \,|\, f(t)) \tag{B1}$$

so that

$$\frac{\partial g_B}{\partial t} = \frac{\partial g_B}{\partial f} \frac{df}{dt} \; . \tag{B2}$$

In the leading-order Bogoliubov result, we make use of the fact that the variation of f with time is slow, of order ϵ, and we expand g in a power series in ϵ,

$$g_B = g_B^{(0)} + \epsilon g_B^{(1)} + \epsilon^2 g_B^{(2)} + \cdots \; . \tag{B3}$$

Note that $\partial f/\partial t$ is expanded but, in contrast, f is not expanded. Thus, the equations for f and g, i.e., Eqs. (3) and (4), in lowest order reduce to

$$\frac{df_B}{dt} = -\epsilon \int dx \, \delta(x) g_B^{(0)}(x \,|\, f(t)) \; , \tag{B4}$$

$$\frac{\partial g_B^{(0)}}{\partial x} = \delta(x) f_B \; . \tag{B5}$$

By direct substitution, it follows that the leading-order Bogoliubov results given in Eqs. (11) and (12) are solutions to Eqs. (B4) and (B5). In the Bogoliubov derivation of the Boltzmann equation, it is the leading-order result for the correlation function that is used. However, in order to fully investigate the value of the Bogoliubov method, we have determined the functions f_B and g_B when the entire Bogoliubov series for g_B is summed. This result can be obtained by solving directly for g_B. When the Bogoliubov condition in Eq. (B2) is employed and g_B is not expanded, the equations for f and g, i.e., Eqs. (3) and (4), reduce to

$$\frac{df_B}{dt} = -\epsilon \int dx \, \delta(x) g_B(x \,|\, f) \; , \tag{B6}$$

$$\left(\frac{\partial g_B}{\partial f_B} \right) \frac{df_B}{dt} + \frac{\partial g_B}{\partial x} = \delta(x) f_B \; . \tag{B7}$$

Clearly, the results given in Eqs. (9) and (10) satisfy Eqs. (B6) and (B7). In all our expressions for f we have used the normalization $f(0) = 1$. In addition, Bogoliubov imposes the condition

$$\lim_{\lambda \to \infty} g_B(x - \lambda, \; t) = 0 \; . \tag{B8}$$

This condition is always satisfied since there is no contribution to g prior to the collision of the light particle with the heavy particle located at the origin. Note that this property holds for both g and g_B.

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[26]The results given in this paper for the soluble model are in complete agreement with the asymptotic results obtained previously for the f and g equations of the BBGKY hierarchy. For example, compare Eq. (7) of this paper with Eq. (7) of Ref. 22.

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Absorption Spectrum of Cd I Vapor at 30 Å Using the Background Radiation of the 2.5-GeV Bonn Synchrotron

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New resonances have been observed in the absorption spectrum of neutral cadmium vapor at wavelengths around 30 Å. These are believed to be at present the shortest-wavelength metal-vapor absorption features recorded optically. The 2.5-GeV electron synchrotron at Bonn University was used as a background source of continuous radiation. Hartree-Fock calculations enabled identification of the resonances as caused by excitation from the $3d$ shell, although somewhat larger differences between computed and observed wavelengths were found than were expected.

Following our previous work on the absorption spectra of metal vapors[1–6] and the work recently published by Ederer, Lucatorto, and Madden[7] on the Li I absorption spectrum, we report here absorption features caused by excitation of a $3d$ inner-shell electron in Cd I vapor, the structure being more than 400 V above the first ionization potential of Cd I. Our results were obtained in a collaborative experiment between the European Space Research Institute and the Synchrotron Group of the Physikalisches Institut at the University of Bonn.

In some earlier work[2,5] using the Baloffet, Romand, and Vodar (BRV) source[8] to provide a background radiation continuum, spectra of alkali-metal vapors were recorded down to 180 Å. At wavelengths below about 100 Å, the BRV continuum became too weak to record absorption spectra. The furnace design used in Ref. 2 allowed a metal-vapor pressure of several Torr to be achieved in the central region of the furnace while maintaining a pressure of about 10^{-4} Torr at the ends, but did not meet the much more stringent requirements (vacuum better than 10^{-6} Torr) for operation on a synchrotron.

Ederer, Lucatorto, and Madden[7] have used a heat-pipe furnace system together with 1000-Å-thick aluminum windows to contain Li vapor at pressures of up to 2 Torr. With this apparatus, they were able to study the Li I absorption spectrum between 170 and 210 Å using the background radiation continuum of the National Bureau of Standards 180-MeV synchrotron. They were not, however, able to observe structures much below 170 Å, because of the L_{23} cutoff in the aluminum filters.

We have further developed the furnace described in Ref. 2, essentially by increasing the efficiency of the vapor trapping system. Details of our arrangement will be published separately. Spectra were recorded up to temperatures corresponding to a Cd vapor pressure of 3 Torr at the center of the furnace, the over-all length of the furnace being about 1.5 m. However, owing to the steep pressure gradients in the trapping system, the pressure-path product is probably much smaller than these figures would indicate. Our spectra were recorded using a 2-m grazing incidence spectrograph[9] equipped with a 1200-line/mm Bausch and Lomb platinized replica grating, the entrance slit being set for a 2-deg grazing angle. The slit width was 6.3 μ. The spectrograph had been focussed down to 26 Å on a low-inductance spark source at the European Space Research Institute in Frascati. It was constructed around a vacuum chamber and Rowland circle made by Hilger and Watts Ltd., the supporting frame being demountable for ease