Generalized Bogoliubov hypothesis for dense fluids

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The Bogoliubov prescription relevant to the equilibration of a gas is reformulated to describe dense fluids. The revised description assumes that in the "kinetic state" of a dense fluid, multiparticle distribution functions are functionals of the one- and two-particle distribution functions. This principle is applied to the Bogoliubov-Born-Kirkwood-Green-Yvon (BBKGY) sequence and a closed kinetic equation for the radial distribution function, $g(\vec{x},\vec{p},t)$, is obtained relevant to a homogeneous, anisotropic fluid, where $\vec{x}$ and $\vec{p}$ are relative two-particle displacement and momentum, respectively. In the equilibrium limit the kinetic equation reduces to a linear integro-differential equation. A closed solution to this equation is obtained in operational form which, in the limit of weak interactions, reduces to the canonical exponential form, and, with interactions turned off, gives the correct unit value of g. These equilibrium equations are applied to the specific configuration of a fluid whose particles interact under point repulsion and Newtonian attraction. Asymptotic expressions for the radial distribution function for large and small values of interparticle displacement give oscillatory decay to unity and vanishing decay to zero, respectively. These findings are consistent with previously described behavior of the radial distribution.

I. INTRODUCTION

In Bogoliubov's description[1-4] of the evolution of a gas to equilibrium, there are three periods of development: initial, kinetic, and hydrodynamic. It is assumed that in the kinetic stage, multiparticle distribution functions are functionals of the one-particle distribution.

Rosenbluth and Rostoker[5] applied this ansatz to a weakly coupled plasma in derivation of the Vlasov equation.[6,7] The Bogoliubov hypothesis was employed by various authors in developing generalizations of the Boltzmann equation to denser configurations.[8-10]

In the present study, the Bogoliubov prescription is reformulated to describe dense fluids where correlation between particles is important. Our hypothesized extension of Bogoliubov's principle reads as follows: In the kinetic stage of evolution of a dense fluid, multiparticle distribution functions are functionals of the one- and two-particle distribution functions.

This principle evidently remains in the spirit of Bogoliubov's original ansatz. Furthermore, we note that Kirkwood's classical superposition approximation[11,12] is likewise in keeping with the proposed generalization.

In the present study this principle is applied in derivation of a kinetic equation for the radial distribution function relevant to a moderately dense fluid. Specifically, the fluid is assumed to be homogeneous but anisotropic. Furthermore, it is assumed that the fluid is in a near-equilibrium state. This assumption permits a symmetry argument to be applied to interaction integrals which simplifies the resulting equation of motion.

It is hypothesized that for the given state of the fluid, appropriate independent variables are $\vec{x}$, $\vec{p}$, and t, where $\vec{x}$ is relative two-particle displacement, $\vec{p}$ is relative two-particle momentum, and t is time. This assumption is borne out by the form of the derived equation.

Various well-known conditions on the radial distribution function come into play in the analysis. These are as follows:[13]

(a) $g(\vec{x},\vec{p},t)\rightarrow g(x)$, equilibrium;
(b) $g(x)\simeq\exp[-u(x)/k_BT]$, weak coupling;
(c) $g(x)\sim 1$, as $x\rightarrow\infty$;
(d) $g(0)=0$; and
(e) $g(x)=1$, no interactions.

In the equilibrium limit the kinetic equation for $g(\vec{x},\vec{p},t)$ reduces to an integro-differential equation for $g(x)$. A closed solution for this equation is given in operational form which, in the limit of weak interactions, returns the canonical exponential form (b) whereas in the absence of interactions the solution yields the correct unit value (e).

These equilibrium equations are applied to the specific configuration of a fluid whose particles interact under point repulsion and Newtonian attraction. A differential equation is obtained for the radial distribution function which contains irregular singularities at the origin. The form of the general solution to this equation is described and asymptotic expressions are obtained for the solution in domains of large and small interparticle separation. These expressions exhibit oscillatory decay to unity and vanishing decay to zero, respectively, consistent with previously described behavior of this distribution. Further discussion of the initial and hydrodynamic stages together with an overview of these extended descriptions relevant to dense fluids are presented at the close of the paper.

II. ANALYSIS

A. Mayer expansion

In the description of dense fluids it is appropriate to work with correlation functions as opposed to joint multiparticle distribution functions. Thus let $F_s(1,\ldots,s)$ denote the joint s-particle distribution function with normalization

$$\int F_s(1,\ldots,s)d1\cdots ds=1\ . \tag{1}$$

Correlation functions are then obtained through the Mayer expansions[14]

$$\begin{aligned} &F_2(1,2)=F_1(1)F_1(2)+C_2(1,2)\ ,\\ &F_3(1,2,3)=F_1(1)F_1(2)F_1(3)\\ &\qquad\qquad+\sum_{P(1,2,3)}F_1(1)C_2(2,3)+C_3(1,2,3)\ ,\\ &\ldots\ . \end{aligned} \tag{2}$$

In this expression $P(1,2,3)$ denotes permutation of the three integers. The preceding notation is such that "1" represents the phase variables $\vec{x}_1,\vec{p}_1$, where $\vec{x}$ and $\vec{p}$ are displacement and momentum, respectively.

B. Equations of motion

We consider an aggregate of N neutral molecules of mass m confined to the volume V. The sth equation of the Bogoliubov-Born-Kirkwood-Green-Yuon (BBKGY) hierarchy (called BY_s) is given by[2]

$$\left[\frac{\partial}{\partial t}+\sum_{i=1}^{s}\vec{p}_i\cdot\frac{\partial}{\partial\vec{x}}+\alpha\sum_{j=1}^{s}\sum_{\substack{i=1\\ i<j}}^{s}\vec{G}_{ij}\cdot\left[\frac{\partial}{\partial\vec{p}_i}-\frac{\partial}{\partial\vec{p}_j}\right]\right]F_s$$
$$=-\frac{\alpha}{4\pi\gamma}\sum_{i=1}^{s}\frac{\partial}{\partial\vec{p}_i}\cdot\int d(s+1)\vec{G}_{i,s+1}F_{s+1}\ . \tag{3}$$

Parameters occurring in this equation are defined as follows:

$$\alpha\equiv\Phi_0/k_BT,\quad \frac{1}{\gamma}\equiv4\pi nr_0^3,\quad n\equiv N/V\ . \tag{3a}$$

Variables in (3) are related to reduced valuables according to

$$\begin{aligned} &\bar{\vec{x}}=r_0\vec{x},\quad \bar{\vec{p}}=mC\vec{p},\quad mC^2=k_BT\ ,\\ &\bar{\vec{G}}_{ij}=\frac{\Phi_0}{r_0}\vec{G}_{ij},\quad \bar{t}=\frac{r_0}{C}t\ . \end{aligned} \tag{3b}$$

Barred variables are dimensional (i.e., carry units). These relations serve to identify the strength and range of potential, Φ_0 and r_0, respectively. The interaction force on particle i due to particle j is $\vec{G}_{ij}$. The distribution function in (3) is similarly rewritten as

$$F_s=(mC)^{3s}V^s\bar{F}_s\ . \tag{3c}$$

It proves convenient to introduce the *interaction parameter*[15]

$$\eta^2\equiv\frac{\alpha}{\gamma}\ . \tag{4}$$

Thus the coefficient that multiplies the integral term in (5) may be written $\eta^2/4\pi$. An interpretation of this parameter is revealed through introduction of the term

$$\mathcal{N}\equiv4\pi nr_0^3 \tag{5}$$

which permits the relation

$$\eta^2\equiv\frac{\mathcal{N}^2\Phi_0}{\mathcal{N}k_BT}\ . \tag{6}$$

We may therefore identify η^2 with the ratio of pair interaction energy to thermal energy in the range volume, $\sim r_0^3$. The parameter η^2 may therefore be taken as a measure of the degree to which the fluid is strongly coupled.

The BY_s as given by (3) may be rewritten in the more concise form

$$\left[\frac{\partial}{\partial t}+\hat{K}_s+\alpha\hat{B}_s\right]F_s=-\frac{\eta^2}{4\pi}\hat{I}_sF_{s+1}\ . \tag{7}$$

The operators $\hat{K}_s$, $\hat{B}_s$, and $\hat{I}_s$ follow by identification with parallel terms in (3). Substituting the expansion (2) into (7) gives the following forms for BY_1 and BY_2:

$$\left[\frac{\partial}{\partial t}+\hat{K}_1\right]F_1(1)=-\frac{\eta^2}{4\pi}\hat{I}_1[F_1(1)F_1(2)+C_2(1,2)]\ , \tag{8}$$

$$\begin{aligned} &\left[\frac{\partial}{\partial t}+\hat{K}_2+\alpha\hat{B}_2\right][F_1(1)F_1(2)+C_2(1,2)]\\ &\quad=-\frac{\eta^2}{4\pi}\hat{I}_2\left[F_1(1)F_1(2)F_1(3)+\sum_{P(1,2,3)}F_1(1)C_2(2,3)\right.\\ &\qquad\qquad\left.+C_3(1,2,3)\right]\ . \end{aligned} \tag{9}$$

C. Moderately dense fluids

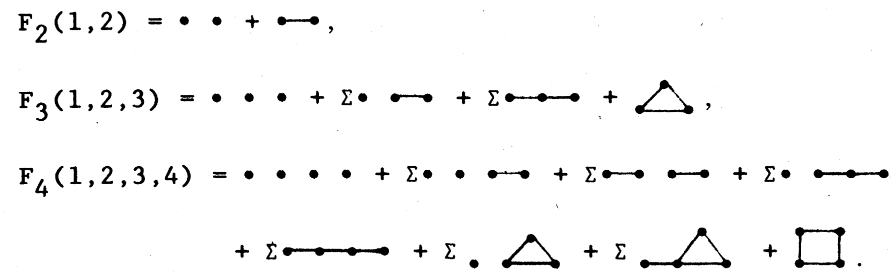
Working with correlation functions, our proposed description of the kinetic stage of a dense fluid asserts that higher-order correlation functions, $C_s(1,2,\ldots,s)$, $s>2$, are functionals of $C_2(1,2)$. Application of this statement in the present work is well described with the aid of the following diagrammatic representation:

$F_1(1)F_1(2)\equiv$ • • ,

$C_2(1,2)\equiv$ •—• ,

$C_2(1,2)C_2(2,3)\equiv$ •—•—• .

In accord with our extended Bogoliubov principle, the Mayer expansion (2) is written in terms of two-body correlations only, as described by the following equations:

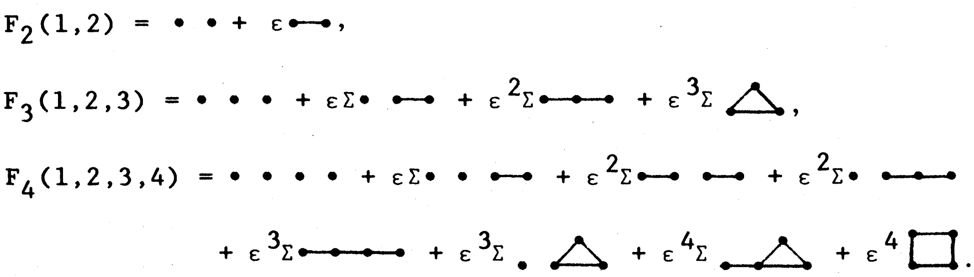


(10)

Summations are over permutation of particle numbers.

Note that corresponds to the Kirkwood superposition $F_3(1,2,3)=C_2(1,2)C_2(2,3)C_2(3,1)$.

A moderately dense fluid may be described by the following scheme. We introduce a parameter of smallness ϵ, and weight the correlation coupling, , with ϵ. In this representation the preceding expansions assume the form



(11)

Sufficiently close to equilibrium we assume homogeneity and that the time dependence of $F_2(1,2)$ is contained primarily in $C_2(1,2)$.[16] Accordingly we set $F_1(1)=F_1(\vec{p}_1)$. The relation (8) then gives the constraint

$$\hat{I}_1 C_2(1,2)=0 \; . \tag{12}$$

With coupling parameters η^2 and α taken to be $O(1)$ and keeping terms to $O(\epsilon)$ in (11), substitution into (9) gives the following equation of motion for $C_2(2,3)$. Here we are writing F for $F_1(1)$:

$$\left[\frac{\partial}{\partial t}+\hat{K}_2\right]C_2(1,2)+\alpha\hat{B}_2[F(\vec{p}_1)F(\vec{p}_2)+C_2(1,2)] = -\frac{\eta^2}{4\pi}\hat{I}_2 \sum_{P(1,2,3)} F(\vec{p}_1)C_2(2,3) \; . \tag{13}$$

A more tractable reduced equation stemming from the preceding relation follows below.

D. Total correlation function

Near equilibrium we further assume that $C_2(1,2)$ has the form

$$C_2(1,2)=F(\vec{p}_1)F(\vec{p}_2)h(\vec{x},\vec{p},t) \; , \tag{14}$$

where h is called the "total" correlation function.[13,17] It is related to the "radial distribution function" as

$$h(1,2)\equiv g(1,2)-1 \; . \tag{15}$$

The variables $\vec{x}$ and $\vec{p}$ in (14) are defined through the change in variables

$$\vec{x}=\vec{x}_1-\vec{x}_2, \quad \vec{p}=\vec{p}_1-\vec{p}_2 \; ,$$
$$\vec{X}=\tfrac{1}{2}(\vec{x}_1+\vec{x}_2), \quad \vec{P}=\tfrac{1}{2}(\vec{p}_1+\vec{p}_2) \; . \tag{16}$$

Thus $\vec{X}$ and $\vec{P}$ may be identified with the displacement and momentum of the center of mass of the two-particle system.

It should be noted at this point that the specific dependence of h on its independent variables is hypothesized. This choice of dependence must be corroborated by the form of our final equation of motion for h. Note in particular that the hypothesized $\vec{x}$ dependence of h relates to invariance under translation in coordinate space. The $\vec{p}$ dependence relates to invariance under translation in momentum space, which in the present instance is equivalent to Galilean invariance.

Discrete operators in (13) have the form

$$\hat{K}_2 C_2(1,2)=F(\vec{p}_1)F(\vec{p}_2)\vec{p}\cdot\frac{\partial}{\partial\vec{x}}h(\vec{x},\vec{p},t) \; , \tag{17a}$$

$$\hat{B}_2 C_2(1,2)=\vec{G}_{12}\cdot\left[F(\vec{p}_2)\frac{\partial}{\partial\vec{p}_1}F(\vec{p}_1)-F(\vec{p}_1)\frac{\partial}{\partial\vec{p}_2}F(\vec{p}_2)\right]h + 2F(\vec{p}_1)F(\vec{p}_2)\vec{G}_{12}\cdot\frac{\partial h}{\partial\vec{p}} \; . \tag{17b}$$

In (17a) we set $\partial h/\partial\vec{X}=0$ owing to assumed homogeneity.

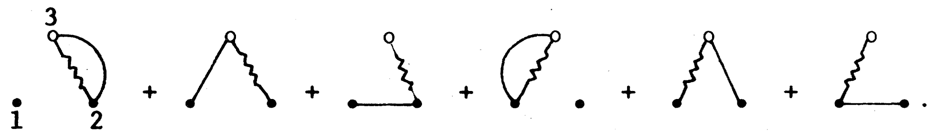
E. Diagrammatic reduction of $\hat{I}_2$

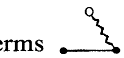
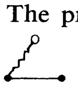
The interaction term in (13) has the explicit representation

$$\hat{I}_2 \sum_{P(1,2,3)} F(1)C_2(2,3)=\sum_{q=1}^{2}\sum_{P(1,2,3)}\frac{\partial}{\partial \vec{p}_q}\cdot\int d3\,\vec{G}_{q3}F(\vec{p}_1)C_2(2,3)\ . \tag{18}$$

We may represent the terms in this sum by diagrams. With represented interaction and representing correlation and o representing the integration variable (3), we have

$$\hat{I}_2 \sum_{P(1,2,3)} F(1)C_2(2,3)= \tag{19}$$

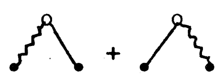


The property that the integral of an isotropic vector field vanishes serves to remove the separable terms  and  leaving four terms in the sum (19).

The constraint condition (12) corresponds to the diagram

$\hat{I}_1 C_2(1,2)=$  .

This identification serves to remove two related terms in (19) leaving

$\hat{I}_2 \sum_{P(1,2,3)} F(1)C_2(2,3)=$ 

$$=\frac{\partial}{\partial \vec{p}_1}F(\vec{p}_1)F(\vec{p}_2)\cdot\int d3\,\vec{G}_{31}h(2,3)F(\vec{p}_3)+\frac{\partial}{\partial \vec{p}_2}F(\vec{p}_1)F(\vec{p}_2)\cdot\int d3\,\vec{G}_{23}h(3,1)F(\vec{p}_3)\ . \tag{20}$$

It should be noted that the preceding diagrams primarily describe coordinate integration. Concentrating for the moment on this component of integration we write

$$I_a=\int d\vec{x}_3\vec{G}_{31}(x_{31})h(\vec{x}_{23},\vec{p}_{23})\ , \tag{21a}$$

$$I_b=\int d\vec{x}_3\vec{G}_{23}(x_{23})h(\vec{x}_{31},\vec{p}_{31})\ . \tag{21b}$$

With the aid of the triangle equality

$$\vec{x}_{13}+\vec{x}_{21}+\vec{x}_{32}=0 \tag{22}$$

(21a) may be written

$$\begin{aligned} I_a&=\int d\vec{x}_{32}\vec{G}_{31}(\,|\vec{x}_{12}-\vec{x}_{32}|\,)h(-\vec{x}_{32},-\vec{p}_{32})\ ,\\ I_a&=\int d\vec{\rho}\,\vec{G}_{31}(\,|\vec{x}-\vec{\rho}|\,)h(-\vec{\rho},-\vec{p})\ . \end{aligned} \tag{23a}$$

In like manner we find

$$\begin{aligned} I_b&=\int d\vec{x}_{31}\vec{G}_{23}(\,|\vec{x}_{12}+\vec{x}_{31}|\,)h(\vec{x}_{31},\vec{p}_{31})\ ,\\ I_b&=\int d\vec{\rho}\,\vec{G}_{23}(\,|\vec{x}+\vec{\rho}|\,)h(\vec{\rho},\vec{p})\ . \end{aligned} \tag{23b}$$

Now note that

$$\begin{aligned} \vec{G}_{31}&=-\vec{G}_{13}=+\frac{\partial}{\partial \vec{x}_1}u(x_{13})\\ &=\frac{\partial}{\partial \vec{x}_1}u(\,|\vec{x}_{12}+\vec{x}_{23}|\,)\\ &=\frac{\partial}{\partial \vec{x}}u(\,|\vec{x}-\vec{\rho}|\,)\ ,\\ \vec{G}_{23}&=-\frac{\partial}{\partial \vec{x}_2}u(x_{23})=-\frac{\partial}{\partial \vec{x}_2}u(\,|\vec{x}_{12}+\vec{x}_{31}|\,)\\ &=+\frac{\partial}{\partial \vec{x}}u(\,|\vec{x}+\vec{\rho}|\,)\ . \end{aligned} \tag{24}$$

Equation (23) may then be rewritten

$$\vec{I}_a=\frac{\partial}{\partial \vec{x}}\int d\vec{\rho}\,u(\,|\vec{x}-\vec{\rho}|\,)h(-\vec{\rho},-\vec{p})\ ,$$

$$\vec{I}_b=\frac{\partial}{\partial \vec{x}}\int d\vec{\rho}\,u(\,|\vec{x}+\vec{\rho}|\,)h(\vec{\rho},\vec{p})\ .$$

Changing variables in I_a as $\vec{\rho}\to\vec{\rho}\,'=-\vec{\rho}$ and assuming that h is a symmetric function of $\vec{p}$, we find

$$\vec{I}_a=-\vec{I}_b\ . \tag{25}$$

The remaining momentum integrals are

$$\mathscr{I}_a = \int d\vec{p}_3 h(\vec{p}_{32}) F(\vec{p}_3) ,$$
$$\mathscr{I}_b = \int d\vec{p}_3 h(\vec{p}_{31}) F(\vec{p}_3)$$

which may be rewritten

$$\begin{aligned} \mathscr{I}_a &= \int d\vec{p}_{32} h(\vec{p}_{32}) F(\vec{p}_{32}+\vec{p}_2) \\ &= \int d\vec{p}\, h(\vec{p}) F(\vec{p}+\vec{p}_2) , \\ \mathscr{I}_b &= \int d\vec{p}\, h(\vec{p}) F(\vec{p}+\vec{p}_1) . \end{aligned} \tag{26}$$

Thus in general, (25) cannot be extended to the momentum component of $\hat{I}_2$. Furthermore, the isolated $\vec{p}_1$ and $\vec{p}_2$ dependencies in $\mathscr{I}_a$ and $\mathscr{I}_b$ appear to violate our hypothesis concerning the arguments of h. However, at equilibrium, $h(\vec{x},\vec{p}) = h(\vec{x})$ and $\mathscr{I}_a = \mathscr{I}_b$. Thus, sufficiently close to equilibrium, in the spirit of (11), we assume

$$\mathscr{I}_a = \mathscr{I}_b + \epsilon^2 \Delta_{ab} , \tag{27}$$

where $\Delta_{ab} \simeq O(1)$, and within the present approximation we write

$$\mathscr{I}_a = \mathscr{I}_b = \int d\vec{p}\, F(\vec{p}) h(\vec{p}) . \tag{28}$$

Note in particular that this assumption renders $\hat{\vec{\Gamma}} h$ independent of $\vec{p}$. Expressions for $\hat{\vec{\Gamma}} h$ for typical intermolecular force laws are tabulated in Appendix A.

III. KINETIC EQUATION FOR $h(\vec{x},\vec{p},t)$ and $g(\vec{x},\vec{p},t)$

A. Equation of motion

Substituting the preceding results into (20) gives

$$\hat{\vec{I}}_2 \sum_{P(1,2,3)} F(1) C_2(2,3) = - \left[\frac{\partial}{\partial \vec{p}_1} FF - \frac{\partial}{\partial \vec{p}_2} FF \right] \cdot \hat{\vec{\Gamma}} h , \tag{29}$$

where

$$\hat{\vec{\Gamma}} h = \int \int d\vec{\rho}\, d\vec{p}\, F(\vec{p}) \vec{G}(|\vec{\rho}+\vec{x}|) h(\vec{\rho},\vec{p}) . \tag{29$'$}$$

With reference to (24) we may also write

$$\hat{\vec{\Gamma}} h \equiv \frac{\partial}{\partial \vec{x}} \hat{\Lambda} h = \frac{\partial}{\partial \vec{x}} \int \int d\vec{\rho}\, d\vec{p}\, F(\vec{p}) u(|\vec{\rho}+\vec{x}|) h(\rho,\vec{p}) . \tag{29$''$}$$

Introducing the operator

$$\hat{\vec{O}} \equiv \frac{\partial}{\partial \vec{p}_1} - \frac{\partial}{\partial \vec{p}_2} = 2 \frac{\partial}{\partial \vec{p}}$$

and combining preceding results gives

$$\begin{aligned} FF \left[\frac{\partial h}{\partial t} + \vec{p} \cdot \frac{\partial}{\partial \vec{x}} h \right] + \alpha \vec{G}(x) \cdot \hat{\vec{O}} FF \\ + \alpha FF \vec{G}(x) \cdot \hat{\vec{O}} h + \alpha \vec{G} \cdot h \hat{\vec{O}} FF + \frac{\eta^2}{4\pi} \hat{\vec{O}} \cdot FF \hat{\vec{\Gamma}} h = 0 . \end{aligned} \tag{30}$$

Our last assumption states that sufficiently near equilibrium, the single-particle distribution has the Maxwellian property

$$\frac{\partial}{\partial \vec{p}_i} F(p_i) = -\vec{p}_i F(p_i) \quad (i=1,2) \tag{31}$$

so that

$$\hat{\vec{O}} FF = -\vec{p} FF \tag{32}$$

and (28) reduces to

$$\left[\frac{\partial}{\partial t} + \vec{p} \cdot \frac{\partial}{\partial \vec{x}} + \alpha \vec{G} \cdot \left[2 \frac{\partial}{\partial \vec{p}} - \vec{p} \right] \right] h + \frac{\eta^2}{4\pi} \vec{p} \cdot \hat{\vec{\Gamma}} h = \alpha \vec{p} \cdot \hat{G} . \tag{33}$$

The transformation (15) converts (33) to the homogeneous equation

$$\begin{aligned} \left[\frac{\partial}{\partial t} + \vec{p} \cdot \frac{\partial}{\partial \vec{x}} + \alpha \vec{G} \cdot \left[2 \frac{\partial}{\partial \vec{p}} - \vec{p} \right] \right] g(\vec{x},\vec{p},t) \\ - \frac{\eta^2}{4\pi} \vec{p} \cdot \hat{\vec{\Gamma}} g(\vec{x},\vec{p},t) = 0 . \end{aligned} \tag{34}$$

Thus with the stated assumptions we have obtained a closed space-time-momentum equation for the radial distribution function which is seen to corroborate our conjecture concerning the arguments of h, or equivalently, g.

Here is a brief recapitulation of assumptions leading to (34).

(a) $g(\vec{x},\vec{p},t)$ is symmetric in $\vec{p}$.
(b) $\mathscr{I}_a = \mathscr{I}_b$ (fluid is near equilibrium).
(c) $\partial F / \partial \vec{p} = -\vec{p} F$.
(d) Time dependence of F_2 contained primarily in C_2.
(e) Terms of $O(\epsilon)$ kept in expansion of F_3. (Fluid is moderately dense.)

Note in particular that the interaction term in (34) satisfies the invariance

$$\hat{\vec{\Gamma}} g = \hat{\vec{\Gamma}} (g + A) , \tag{35}$$

where A is a constant. This invariance is a consequence of the radial property of the interparticle force $\vec{G}$, as well as the thermodynamic limit. (See Appendix A.)

Returning for the moment to dimensional notation, (34) assumes the explicit form

$$\begin{aligned} \left[\frac{\partial}{\partial t} + \vec{v} \cdot \frac{\partial}{\partial \vec{x}} + \frac{\vec{G}}{mC^2} \cdot \left[2C^2 \frac{\partial}{\partial \vec{v}} - \vec{v} \right] \right] g \\ + \vec{v} \cdot \frac{\partial}{\partial \vec{x}} \int d\vec{v}\,' d\vec{\rho}\, F(\vec{v}\,') u(|\vec{\rho}+\vec{x}|) g(\vec{\rho},\vec{v}\,',t) . \end{aligned} \tag{34$'$}$$

All variables in this equation are dimensional. Furthermore, we have set $\vec{p} = m\vec{v}$.

B. Equilibrium limit

In Appendix B an argument is presented which rests in part on the boundary condition $g \to 1$, $x \to \infty$, and concludes that (34) implies $\partial g/\partial\vec{p}=0$ in equilibrium. With this conclusion at hand (34) reduces to

$$\vec{p}\cdot\left[\frac{\partial}{\partial\vec{x}}-\alpha\vec{G}+\frac{\eta^2}{4\pi}\hat{\vec{\Gamma}}\right]g=0\ .$$

Since $\vec{p}$ is an arbitrary vector we may conclude

$$\left[\frac{\partial}{\partial\vec{x}}-\alpha\vec{G}+\frac{\eta^2}{4\pi}\hat{\vec{\Gamma}}\right]g=0\ .$$

Setting

$$\frac{\partial}{\partial\vec{x}}=\hat{\vec{x}}\frac{\partial}{\partial x},\quad \vec{G}=\hat{\vec{x}}G,\quad \hat{\vec{\Gamma}}g=\hat{\vec{x}}\Gamma$$

and dotting $\hat{\vec{x}}$ into the preceding equation, we find

$$\left[\frac{\partial}{\partial x}+\alpha\frac{\partial u}{\partial x}\right]g+\frac{\eta^2}{4\pi}\hat{\Gamma}g=0\ . \tag{36}$$

(It is established in Appendix A that for central forces, $\hat{\vec{\Gamma}}g$ is in the $\hat{\vec{x}}$ direction.)

Introducing an integrating factor permits (36) to be written

$$\frac{\partial}{\partial x}(e^{\alpha u}g)=-\frac{\eta^2}{4\pi}e^{\alpha u}\hat{\Gamma}g\ . \tag{37}$$

Integrating from x to ∞ (where we take $u=0$ and $g=1$) gives the linear integral equation

$$(1-e^{-\alpha u}\hat{\Phi})g=e^{-\alpha u}\ . \tag{38}$$

Here we have set

$$\hat{\Phi}\equiv\frac{\eta^2}{4\pi}\int_x^\infty dx'e^{\alpha u(x')}\hat{\Gamma}\ .$$

The solution to (38) may be written in the operational form

$$g(x)=(1-e^{-\alpha u}\hat{\Phi})^{-1}e^{-\alpha u}\ ,$$
$$g(x)=[1+e^{-\alpha u}\hat{\Phi}+(e^{-\alpha u}\hat{\Phi})^2+\cdots]e^{-\alpha u}\ . \tag{39}$$

To lowest order in the coupling parameter η^2 we find

$$g(x)=e^{-\alpha u}\ .$$

In dimensional units this expression returns the canonical result[18]

$$g(x)\simeq e^{-u(\bar{x})/k_BT} \tag{40}$$

which for rigid repulsion at the $\bar{x}=0$ gives the correct boundary condition $g(0)=0$. Furthermore, for no interactions, $u=$const, and (39) again gives the correct result, $g(x)=1$. Thus we find that (36), relevant to moderately dense fluids in equilibrium, returns correct limiting forms for $g(x)$ both in the ideal and weakly coupled limits.

C. Application to a Newtonian fluid

We consider a fluid whose molecules interact under the force

$$\vec{G}(x)=\hat{\vec{x}}\left[\bar{\delta}(x)-\frac{1}{x^2}\right]\ , \tag{41}$$

where $\bar{\delta}(x)$ is a limiting form of the Dirac δ function, defined in (A9), and which represents a point repulsion. The x^{-2} term represents Newtonian attraction.

Substitution of (41) into (36) gives

$$\frac{\partial}{\partial x}g-\frac{\alpha}{x^2}[\delta(x)-1]g+\frac{\eta^2}{x^2}\int_0^x d\rho\rho^2[g(\rho)-1]=0\ . \tag{42}$$

The unit term under the integral stems from the invariance property (35). (See Appendix A.) Note in particular that this unit term serves to maintain a finite value of the integral in the canonical limit $g\to 1$, $x\to\infty$.

Multiplying (42) through by x^2 and differentiating gives

$$g''+\left[\frac{2}{x}+\frac{\alpha}{x^2}\right]g'+\eta^2(g-1)=0 \tag{43}$$

relevant to the domain $0<0_+\le x$. We seek a solution to this equation which gives $g(0)=0$. This value is compatible with the structure of (42) and is physically consistent with the point repulsion at $x=0$.

Changing variables to

$$y\equiv\eta x$$

permits (43) to be rewritten

$$g''+\left[\frac{2}{y}+\frac{k}{y^2}\right]g'+g=1\ , \tag{44}$$
$$k\equiv\alpha\eta\ .$$

The structure of the general solution to this equation is derived in Appendix C.

D. Oscillatory and exponential behavior

Introducing the transformation[19]

$$g(y)=\frac{1}{y}e^{k/2y}v(y)+1$$

in (44) gives the Schrödinger-like equation

$$v''+\left[1-\frac{(k/2)^2}{y^4}\right]v=0\ . \tag{45}$$

We may conclude that for $y^2>k/2$, $g(y)$ is oscillatory whereas for $y^2<k/2$, $g(y)$ is exponential. In the domain $y^2\gg k/2$, (45) gives

$$v=A\cos y+B\sin y$$

which corresponds to

$$g^>(y)=\frac{e^{k/2y}}{y}(A\sin y+B\cos y)+1\ . \tag{46}$$

In the domain $y^2\ll k/2$, (45) reduces to

$$v''-\frac{(k/2)^2}{y^4}v=0$$

which has the solution[20]

$$v(y)=y(Ae^{k/2y}+Be^{-k/2y}) .$$

Converting to $g(y)$ we find

$$g^{<}(y)=Ae^{k/y}+B+1 . \tag{47}$$

Setting $A=0$, $B=-1$ gives the correct starting value $g(0)=0$.

E. General solution and asymptotic expansions

A general property of the solution to (44) is as follows. Let $f(y,k)$ be one solution to the equation. Then the general solution is (see Appendix C)

$$g(y)=A'e^{k/y}f(y,-k)+B'f(y,k)+1 . \tag{48}$$

Furthermore we note that both solutions to (44) are irregular at the origin.[21] However, an asymptotic expansion[22] of the solution may be constructed in this domain and is given by

$$g(y)=1+b_0\left[1-\frac{y^3}{3k}+\frac{y^4}{k^2}+\frac{1}{b_0}\sum_{n=5}^{\infty}b_ny^n\right] . \tag{49}$$

For $n\geq 3$, b_n coefficients obey the divergent recurrence relation

$$-nb_nk=b_{n-3}+n(n-1)b_{n-1} . \tag{49'}$$

Setting $b_0=-1$ returns the correct starting value $g(0)=0$. [Note also that in (49) we have set $A'=0$ and $B'=1$.]

For sufficiently small y, any finite sum of starting terms in (49) is an approximate solution to (44). The error of a solution containing terms up to y^l is $O(y^{l-2})$.

Note also that for $y\gtrsim 0$, (49) gives

$$g'(y)=\frac{y^2}{k}-\frac{4y^3}{k^2}+\cdots ,$$

which gives the correct behavior

$$g'(0_+)>0 . \tag{50}$$

A brief recapitulation of these findings relevant to the interparticle force (41) is as follows.

For large y ($y\gg k/2$), the solution is given by (46):

$$g(y)\sim\frac{e^{k/2y}}{y}(A\sin y+B\cos y)+1 ,\qquad g(y)\sim 1 . \tag{51}$$

For small y ($y\ll k/2$), the solution is given by (49):

$$g(y)\sim\frac{y^3}{3k}-\frac{y^4}{k^2}+\cdots ,\qquad g(y)\sim 0 . \tag{52}$$

F. Nature of solution

The discarded first term in (47) exhibits the well-known singularity of $g(y)$ near the origin relevant to Newtonian fluids.[13,23] In the present study however, the point repulsion at the origin included in (41) imposes the boundary condition stated beneath (43), viz., $g(0)=0$, which leads to the nonsingular starting structure of $g(y)$ given by (52).

For large y, on the other hand, the asymptotic value given by (46), $g(y)\sim 1$, when taken with the potential $u\sim -r^{-1}$ leads to divergent thermodynamic properties [see (53) below].[24]

IV. OVERVIEW OF THE THREE STAGES

To complete our extension of Bogoliubov's description of the equilibration of a fluid, we return to the initial and hydrodynamic stages mentioned previously in the introduction. With C taken as a measure of the mean speed of molecules, the initial stage occurs in the interval $0\leq t\leq r_0/C$, subsequent to perturbation of the fluid away from equilibrium. Together with Bogoliubov, in this interval we assume that in general the state of a fluid is described by no less than the full N-body distribution.

In the final hydrodynamic stage, the Bogoliubov description stipulates that all s-particle distributions ($s\leq N$) are functionals of the first five moments of F_1, i.e., $n,\vec{u},T$, where $\vec{u}$ is macroscopic fluid velocity. For a dense fluid, interparticle potential influences the state of the fluid and the two-body distribution comes into play. This is the underlying reason why the Bogoliubov description of both the kinetic and hydrodynamic stages must be generalized for dense fluids. The role of the interaction potential in dense fluids is evident in the fundamental energy and pressure relations[13,17]

$$\frac{E}{Nk_BT}=\frac{3}{2}+\frac{n}{2k_BT}\int u(r)g(r)4\pi r^2dr , \tag{53a}$$

$$\frac{P}{nk_BT}=1-\frac{1}{6nk_BT}\int u'(r)g(r)4\pi r^3dr . \tag{53b}$$

Thus it is conjectured that in the hydrodynamic stage of a dense fluid, higher-order distributions are functionals of the kinetic moments $(n,\vec{u},T)$ and correlation integrals (E,P).

These conjectured dependencies of F_s of a dense fluid in the three fundamental intervals are summarized below.

Epoch	Description
Initial	$F_N(1,\ldots,N)$
Kinetic	$F_s=F_s(F_1,F_2)$
Hydrodynamic	$F_s=F_s(n,\vec{u},T,E,P)$

V. CONCLUSIONS

In the present work a proposed extension of Bogoliubov's kinetic-theory formulation was given for dense fluids. Primary attention was devoted to the kinetic interval and the extended principle was employed in derivation of a closed kinetic equation for the radial distribution function of a moderately dense fluid which is close to equilibrium. In equilibrium this equation was found to reduce to an integro-differential equation for $g(x)$. An operational solution to this equation returned correct boundary conditions for $g(x)$.

Apart from introducing this generalization of Bogoliubov's description, the main thrust of this analysis was to obtain a kinetic equation for $g(\vec{x},\vec{p},t)$. The equilibrium component of this study was undertaken primarily to support the validity of the derived kinetic equation (34). Nevertheless, some additional worth of this equilibrium analysis occurs from the linearity of the derived equation (36) and the fact that this result stems from first principles, i.e., the Liouville equation. Such derivations which obtain valid equilibrium distributions are of note because starting equations do not imply a preferred direction in time.[2,25]

Equations for the structure of fluids derived in equilibrium statistical mechanics[13,17] (e.g., Born-Green-Yvon, hypernetted chain, Percus-Yevick) all incorporate the *a priori* canonical distribution. The nonlinearity of these equations stems from higher-order correlations and are therefore more appropriate to dense fluids than linear results obtained in the present work.

Finally, our equilibrium results were applied to a fluid whose particles interact under point repulsion and Newtonian attraction. A differential equation was obtained for the radial distribution function. Asymptotic expressions in domains of large and small values of interparticle displacement gave oscillatory decay to unity and vanishing decay to zero, respectively, consistent with previously described behavior of this distribution.

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APPENDIX A: EVALUATION OF INTERACTION INTEGRALS

1. Potentials x^{-N}

In this appendix we list various forms of the interaction terms $\hat{\vec{\Gamma}}g$ and $\hat{\Lambda}g$ appropriate to typical intermolecular force laws. Potentials corresponding to these forces are commonly of the form[26]

$$u(x)=\frac{K_N}{x^N}-\frac{K_M}{x^M},\quad N>M\ . \tag{A1}$$

Thus we examine

$$u_N(x)\equiv\frac{K_N}{x^N} \tag{A2}$$

and look specifically at the space-dependent component of $\hat{\Lambda}g$,

$$\hat{\Lambda}g=\int d\vec{\rho}\,u(\,|\,\vec{x}+\vec{\rho}\,|\,)g(\vec{\rho})\ . \tag{A3}$$

With $\vec{x}$ taken as the polar axis and g assumed isotropic in $\vec{x}$ we write

$$\begin{aligned}\hat{\Lambda}g&=\int_0^\infty 2\pi d\rho\,\rho^2 g(\rho)V(\rho,x)\ ,\\ V(\rho,x)&\equiv\int_{-1}^{1}d\mu\,u(\,|\,\vec{x}+\vec{\rho}\,|\,)\ ,\end{aligned} \tag{A4}$$

where $\cos^{-1}\mu$ is the angle between $\vec{x}$ and $\vec{\rho}$. Substituting (A2) in (A4) gives

$$\frac{V_N(\rho,x)}{K_N}=\int_{-1}^{1}\frac{d\mu}{(x^2+\rho^2+2x\rho\mu)^{N/2}}\ . \tag{A5}$$

For $N=1$ and 2,

$$\begin{aligned}V_1/K_1&=\frac{1}{x\rho}(\,|\,x+\rho\,|-|\,x-\rho\,|\,)\ ,\\ V_2/K_2&=\frac{1}{x\rho}\ln\frac{|\,x+\rho\,|}{|\,x-\rho\,|}\ .\end{aligned} \tag{A6}$$

For $N>2$,

$$V_N/K_N=\frac{1}{(N-2)x\rho}\left[\frac{1}{|\,\rho-x\,|^{N/2}}-\frac{1}{|\,\rho+x\,|^{N-2}}\right]. \tag{A7}$$

An alternative approach which may prove convenient to the ρ integration in (A4) stems from the defining relation for Gegenbauer polynomials [18] $C_n^{(\alpha)}(x)$,

$$\frac{1}{(1-2\rho x+x^2)^\alpha}=\sum_{n=0}^{\infty}\rho^n C_n^{(\alpha)}(x)\ . \tag{A8}$$

Note, in particular, that for $\alpha=\frac{1}{2}$, $C_n^{(\alpha)}$ reduce to Legendre polynomials relevant to the Coulomb potential.

2. Point repulsion

A point repulsion may be represented by the force

$$\vec{G}=\lim_{\epsilon\to 0}\hat{\vec{x}}\delta(x+\epsilon)\equiv\hat{\vec{x}}\overline{\delta}(x)\ , \tag{A9}$$

where $\delta(x)$ is the Dirac delta function. We wish to show that

$$\hat{\vec{\Gamma}}g=0$$

for this interaction. First note that

$$\hat{\vec{\Gamma}}g=\int d\vec{\rho}\,\vec{G}(\,|\,\vec{x}+\vec{\rho}\,|\,)g(\rho)=\int d\vec{\rho}\,\vec{G}(\rho)g(\,|\,\vec{\rho}-\vec{x}\,|\,) \tag{A10}$$

and for $\delta(x)$ in spherical coordinates we write

$$\delta(x)\to\frac{\delta(x)}{x^2}\ .$$

Evaluating the Cartesian coordinates of $\hat{\vec{\Gamma}}g$ with $\vec{x}$ taken as the polar axis we find

$$\hat{\vec{\Gamma}}g=\lim_{\epsilon\to 0}\int\int\int d\phi\, d\cos\theta\, d\rho\, \rho^2(\cos\theta,\sin\theta\sin\phi,\sin\theta\cos\phi)\frac{\delta(\rho+\epsilon)}{(\rho+\epsilon)^2}g[(\rho^2+x^2-2\rho x\cos\theta)^{1/2}] \tag{A11}$$

$$=\lim_{\epsilon\to 0}\left[\hat{\vec{x}}2\pi\int d\cos\theta\cos\theta\, g[(\epsilon^2+x^2+\epsilon x\cos\theta)^{1/2}]\right]$$

$$=\hat{x}\left[2\pi g(x)\int_{-1}^{1}d\cos\theta\cos\theta\right]=\vec{0}\ . \tag{A12}$$

3. Invariance property of $\hat{\vec{\Gamma}}$

We consider the invariance property (35)

$$\hat{\vec{\Gamma}}A=\vec{0}\ , \tag{A13}$$

where A is a constant. This invariance may be obtained from (A10), setting $g=A$. Observing that $\vec{G}$ is isotropic and that the thermodynamic limit is obeyed permits us to write

$$\hat{\vec{\Gamma}}A=A\int d\vec{\rho}\,\vec{G}(\rho)=\vec{0}\ . \tag{A14}$$

The significance of the thermodynamic limit in this argument is that an infinite configuration volume precludes surface effects from altering the isotropy of $\vec{G}$.

Again stemming from (A10), and recalling (24), we write

$$\hat{\vec{\Gamma}}A=A\frac{\partial}{\partial\vec{x}}\int d\vec{\rho}\,u(\rho)=\vec{0}\ . \tag{A15}$$

The infinite volume in this case renders new limits of integration in (A10) independent of x thereby returning (A13).

4. The vector quality of $\hat{\vec{\Gamma}}$

Finally, we wish to establish the relation

$$\hat{\vec{\Gamma}}g=\hat{\vec{x}}\hat{\Gamma}g \tag{A16}$$

TABLE I. Properties of interaction integral;
$\hat{\vec{\Gamma}}g=(\partial/\partial\vec{x})\hat{\Lambda}g$,
$\hat{\Lambda}g=2\pi\int_0^\infty d\rho\,\rho^2 g(\rho)V_N(\rho,x)$,
$V_N/K_N\equiv\int_{-1}^{1}d\mu(x^2+\rho^2+2x\rho\mu)^{-N/2}$.
Interaction potential: $u(x)=K_N/x^N$.

N	V_N/K_N
1	$\frac{1}{x\rho}(\lvert x+\rho\rvert-\lvert x-\rho\rvert)$
2	$\frac{1}{x\rho}\ln\frac{\lvert x+\rho\rvert}{\lvert x-\rho\rvert}$
$N>2$	$\frac{1}{(N-2)x\rho}\left[\frac{1}{\lvert\rho-x\rvert^{N-2}}-\frac{1}{\lvert\rho+x\rvert^{N-2}}\right]$
$\vec{G}=\hat{\vec{x}}\delta(x)$ (point repulsion)	$\hat{\Gamma}g=0$
$g=A$ (A const)	$\hat{\Gamma}A=0$

relevant to radial intermolecular forces. Working in the representation of (A11) gives

$$\hat{\vec{\Gamma}}g=\int\int\int d\cos\theta\, d\phi\, d\rho$$
$$\times\rho^2(\cos\theta,\sin\theta\sin\phi,\sin\theta\cos\phi)$$
$$\times G(\rho)g[(\rho^2+x^2-2\rho x\cos\theta)^{1/2}]\ .$$

Integrating over ϕ removes the "transverse" components of $\hat{\vec{\Gamma}}g$ and returns (A16). The preceding results are listed in Table I.

APPENDIX B: EQUILIBRIUM PROPERTY OF $g(\vec{x},\vec{p})$

We wish to argue that in equilibrium, (34) implies that $\partial g/\partial\vec{p}=0$. We consider the extreme of a gas containing only two particles, or equivalently, a fluid in the weak-coupling limit $\eta=0$. In equilibrium (34) then reduces to

$$\left[\vec{p}\cdot\frac{\partial}{\partial\vec{x}}-\alpha\frac{\partial u}{\partial\vec{x}}\cdot\left[2\frac{\partial}{\partial\vec{p}}-\vec{p}\right]\right]g=0\ . \tag{B1}$$

Substituting the product form

$$g\equiv X(x)Y(p) \tag{B2}$$

into (B1) gives

$$Y\vec{p}\cdot\frac{\partial}{\partial\vec{x}}X-\alpha\frac{\partial u}{\partial\vec{x}}X\cdot\left[2\frac{\partial}{\partial\vec{p}}-\vec{p}\right]Y=0\ .$$

Multiplying through by $\exp(\alpha u)$ permits the first and last terms of the last equation to be combined. There results

$$Y\vec{p}\cdot\frac{\partial}{\partial\vec{x}}(Xe^{\alpha u})+2X\frac{\partial}{\partial\vec{x}}e^{\alpha u}\cdot\frac{\partial}{\partial\vec{p}}Y=0\ . \tag{B3}$$

We assume that Y is isotropic in $\vec{p}$ so that

$$\frac{\partial Y}{\partial\vec{p}}=\hat{\vec{p}}\frac{\partial Y}{\partial p}.$$

Recalling the property

$$\frac{\partial}{\partial\vec{x}}=\hat{\vec{x}}\frac{\partial}{\partial x}$$

then permits (B3) to be written

$$\hat{\vec{x}}\cdot\hat{\vec{p}}\left[Yp\frac{\partial}{\partial x}Xe^{\alpha u}+2X\frac{\partial}{\partial x}e^{\alpha u}\frac{\partial}{\partial p}Y\right]=0\ . \tag{B4}$$

This equation implies

$$\frac{\frac{\partial}{\partial x}Xe^{\alpha u}}{2X\frac{\partial}{\partial x}e^{\alpha u}}=-\frac{\frac{\partial}{\partial p}Y}{pY}=K\ , \tag{B5}$$

where K is a constant. The right-hand equality gives

$$\frac{\partial}{\partial p}Y=-pKY$$

which gives

$$Y=e^{-Kp^2/2}\ . \tag{B6}$$

The left-hand equality of (B5) gives

$$\frac{\partial}{\partial x}Xe^{\alpha u}-2KX\frac{\partial}{\partial x}e^{\alpha u}=0\ ,$$

$$X'+\alpha u'(1-2K)X=0\ ,$$

which gives

$$X=X_0e^{-\alpha(1-2K)u}\ . \tag{B7}$$

Combining (B6) and (B7) we obtain

$$g(x,p)=e^{-\alpha(1-2K)u}e^{-Kp^2/2}\ . \tag{B8}$$

Passing to the limit $x\rightarrow\infty$, $u\rightarrow 0$, we find

$$g(x,p)\rightarrow e^{-Kp^2/2}\ .$$

Recalling the boundary condition $g=1$ at $x=\infty$, gives $K=0$, which concludes the argument.

Note in particular that in equilibrium,

$$F_2(1,2)=F_1(p_1)F_1(p_2)g(x)\ .$$

With F_1 as Maxwellian and $g(x)$ given by (B8) and $K=0$ we find, apart from normalization constants,

$$F_2(1,2)=\exp[-H(1,2)/k_BT]\ ,$$

where H is the two-particle Hamiltonian,

$$H(1,2)=\frac{p_1^2+p_2^2}{2m}+u(\,|\vec{x}_1-\vec{x}_2|\,)$$

and all variables are dimensional.

In the context of this derivation we note that it has been previously established[27] that factorization of the N-particle distribution function into momentum and coordinate products, together with a summational property of kinetic energy, are sufficient to obtain the canonical distribution from the N-body Liouville equation.

APPENDIX C: PROPERTIES OF GENERALIZED EQUATION OF MOTION

In this appendix we examine properties of a generalization of (44)

$$h''+\left[\frac{2}{y}+\frac{k}{y^2}\right]h'+Qh=0\ . \tag{C1}$$

Here we have set

$$h=g-1$$

and Q is an arbitrary function of y.

First note that

$$\Phi(y)=y^2e^{k/y} \tag{C2}$$

is an integrating factor of (C1) which permits it to be rewritten

$$(h'\Phi)'+hQ\Phi=0\ . \tag{C3}$$

In particular,

$$\tilde{h}\equiv\Phi^{-1},\quad \tilde{h}=Ce^{k/y} \tag{C4}$$

gives $(\tilde{h}\Phi)'=0$. This property suggests a trial solution of the form

$$h=\tilde{h}f\ . \tag{C5}$$

Substitution into (C1) gives

$$f''+\left[\frac{2}{y}-\frac{k}{y^2}\right]f'+Qf=0\ . \tag{C6}$$

We may conclude that if

$$h(y)=f(y,k)$$

is a solution to (C1), then

$$\tilde{h}(y)=Ce^{k/y}f(y,-k) \tag{C7}$$

is also a solution. Thus we find that the general solution to (C1) is given by

$$h(y)=B'f(y,k)+A'e^{k/y}f(y,-k)\ . \tag{C8}$$

With Q regular at the origin, rules established by Ince[21] indicate that, at most, (C1) has one regular solution at the origin. [This is evident from (C8).] However, Taylor-series substitution into (C1) gives the divergent series (49). We may conclude that both solutions of (C1) are irregular at the origin.

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