Time-Reversed Motion in Kinetic Theory*

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A set of reversible equations for F_1, the first distribution function and g, the correlation function, are derived for the weak force case. The "forward motion," i.e., development in time from uncorrelated initial conditions, and the corresponding reverse motion are examined. In the "forward motion" the equation for F_1 evolves into the Fokker-Planck equation while in the corresponding reverse motion F_1 is described by an anti-Fokker-Planck equation.

I. INTRODUCTION

THE problem of irreversibility has existed since the time of Boltzmann. The problem may be stated as: How can one derive an irreversible equation (e.g., the Boltzmann equation, the Fokker-Planck equation) on the basis of reversible mechanics? In recent years a number of derivations of irreversible equations have been accomplished based on a variety of assumptions. However, these methods have not completely illuminated the transition from the reversible to the irreversible equations. Most of these methods start from the Bogoliubov-Born-Green-Kirkwood-Yvon (BBKGY) equations,[1] which for an infinite system are

$$\frac{\partial F_s(x_1,\cdots x_s,t)}{\partial t}+\mathcal{H}_sF_s(x_1,\cdots x_s,t)=\frac{1}{v}\int dx_{s+1}\sum_{i\leq s}\theta_{i,s+1}F_{s+1}(x_1,\cdots x_{s+1},t)\quad(1)$$

$$s=1,2,\cdots,$$

where $x_i\equiv\{\mathbf{q}_i,\mathbf{p}_i\}$; $\mathbf{q}_i$, $\mathbf{p}_i$ being the position and momentum of the ith particle,

$$\theta_{ij}\equiv\frac{\partial\varphi_{ij}}{\partial\mathbf{q}_i}\cdot\frac{\partial}{\partial\mathbf{p}_i}+\frac{\partial\varphi_{ij}}{\partial\mathbf{q}_j}\cdot\frac{\partial}{\partial\mathbf{p}_j}$$

and $\varphi_{ij}(|\mathbf{q}_i-\mathbf{q}_j|)$ is the intermolecular potential. $\mathcal{H}_s$ is given by

$$\mathcal{H}_s(x_1,\cdots x_s)\equiv\sum_{i=1}^{s}\frac{\mathbf{p}_i}{m}\cdot\frac{\partial}{\partial\mathbf{q}_i}-\sum_{i<j}^{s}\theta_{ij},$$

and v is the volume per particle. F_s is defined through $D_N(x_1,\cdots x_N,t)$ the probability distribution in Γ space for the entire system by

$$F_s(x_1,\cdots x_s,t)=V^s\int\cdots\int D_N(x_1,\cdots x_N,t)dx_{s+1}\cdots dx_N.\quad(2)$$

The sth equation of (1) is obtained by integrating the Liouville equation

$$(\partial D_N/\partial t)+\mathcal{H}_ND_N=0\quad(3)$$

over the coordinates $x_{s+1},\cdots,x_n$.

In particular, the method of Bogoliubov[2] is to assume that all $F_s(s\geqslant 2)$ are functionals of F_1, and the form of the functionals are determined by an assumed boundary condition on the functionals. On this basis, the first BBKGY equation [Eq. (1), $s=1$] becomes the Boltzmann equation (or the Fokker-Planck equation depending on whether the expansion parameter for the distribution function is v^{-1} or the strength of the interaction). The assumptions of Bogoliubov obscure the transition from the set of reversible equations (1) to the irreversible equations. In fact Cohen and Berlin[3] have shown that, on the basis of an equally plausible boundary condition on the functionals, the collision term will be the negative of the Boltzmann collision term (an anti-Boltzmann equation). On the other hand, Green and Piccirelli[4] have shown that, on the basis of a product type condition on $F_s(s\geqslant 2)$ at *the initial time*, the higher distribution functions do, in the course of time, become the functionals of F_1 predicted by Bogoliubov. From this point of view it is no longer important that the Boltzmann equation is time irreversible since the Boltzmann equation evolves from the first BBKGY equation only after some period of time providing the initial $F_s(s\geqslant 2)$ fall within the assumed class of initial conditions. The reverse motion is presumably accomplished, since the BBKGY equations are reversible, by another special class of initial $F_s(s\geqslant 2)$; this motion is probably describable by a single equation for F_1 (such as the anti-Boltzmann equation).[5,6] It is to these points that this paper is devoted.

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

[2] N. N. Bogoliubov, *Problems of a Dynamical Theory in Statistical Physics*, translation by E. K. Gora, *Studies in Statistical Mechanics* (North-Holland Publishing Company, Amsterdam, 1962).

[3] E. G. D. Cohen and T. H. Berlin, Physica **26**, 717 (1960).

[4] M. S. Green and R. A. Piccirelli, Phys. Rev. **132**, 1388 (1963).

[5] There remains the question of how one can justify the use of the Boltzmann equation when other types of developments are possible with other types of initial conditions. The answer must be in the following: If we consider a system in which all that is known initially is F_1, then there exists a large class of initial D_N's that give the same F_1 but different $F_s(s\geqslant 2)$. In the spirit of statistical mechanics we can assign a probability to these D_N's and obtain a probability distribution for F_s and ask for the most

We consider a special case, namely a weak potential in a spatially uniform system. This case is general enough to produce an "irreversible" equation, the Fokker-Planck equation, yet simple enough to examine both the *forward motion* (i.e., the development in time from uncorrelated initial conditions, a special case of the Green and Piccirelli initial condition) and the corresponding *reverse motion*. The evolution of F_1 for the forward motion is governed by the Fokker-Planck equation while the *corresponding* reverse motion is governed by an anti-Fokker-Planck equation.

II. BASIC EQUATIONS

We start our development with the BBKGY equations, Eq. (1), the first two of which, in the spatially uniform case, are

$$\frac{\partial F_1(\mathbf{p}_1,t)}{\partial t}=\frac{1}{v}\int dx_2\theta_{12}(x_1,x_2)F_2(x_1,x_2,t)\,, \tag{4a}$$

$$\frac{\partial F_2(x_1,x_2,t)}{\partial t}+\mathcal{H}_2(x_1,x_2)F_2(x_1,x_2,t) =\frac{1}{v}\int dx_3(\theta_{13}+\theta_{23})F_3(x_1,x_2,x_3,t)\,. \tag{4b}$$

We introduce the two particle, three particle—correlation functions g and h—by

$$F_2(x_1,x_2,t)=F_1(\mathbf{p}_1,t)F_1(\mathbf{p}_2,t)+g(x_1,x_2,t)\,, \tag{5a}$$

$$F_3(x_1,x_2,x_3,t)=F_1(\mathbf{p}_1,t)F_1(\mathbf{p}_2,t)F_1(\mathbf{p}_3,t)+F_1(\mathbf{p}_1,t)g(x_2,x_3,t)+F_1(\mathbf{p}_2,t)g(x_1,x_3,t)+F_1(\mathbf{p}_3,t)g(x_1,x_2,t)+h(x_1,x_2,x_3,t)\,, \tag{5b}$$

etc. With these definitions, Eqs. (4a) and (4b) are

$$\frac{\partial F_1(\mathbf{p}_1,t)}{\partial t}=\frac{1}{v}\int dx_2\theta_{12}g(x_1,x_2,t)\,, \tag{6a}$$

$$\begin{aligned}\frac{\partial g(x_1,x_2,t)}{\partial t}&+[\mathcal{H}_1(x_1)+\mathcal{H}_1(x_2)]g(x_1,x_2,t)\\ &=\theta_{12}[F_1(\mathbf{p}_1,t)F_1(\mathbf{p}_2,t)+g(x_1,x_2,t)]+\frac{1}{v}\int dx_3\theta_{13}F_1(\mathbf{p}_1,t)g(x_2,x_3,t)\\ &\quad+\frac{1}{v}\int dx_3\theta_{23}F_1(\mathbf{p}_2,t)g(x_1,x_3,t)+\frac{1}{v}\int dx_3(\theta_{13}+\theta_{23})h(x_1,x_2,x_3,t)\,.\end{aligned} \tag{6b}$$

Define the operator $S_{-t}(x_1,x_2)$ in terms of the single-particle Liouville operator $\mathcal{H}_1$ by

$$S_{-t}(x_1,x_2)\equiv\exp\{-t[\mathcal{H}_1(x_1)+\mathcal{H}_1(x_2)]\}\,, \tag{7}$$

i.e., $S_{-t}(x_1,x_2)$ when operating on the point x_i ($i=1, 2$) propagates the point back in time along a *free-particle orbit* over a time interval t. Equation (6b) can be formally integrated along free-particle orbits to give

$$\begin{aligned}g(x_1,x_2,t)=S_{-(t-t_0)}(x_1,x_2)g(x_1,x_2,t_0)+\int_0^{t-t_0}dt'S_{-t'}(x_1,x_2)\Big\{&\theta_{12}[F_1(\mathbf{p}_1,\,t-t')F_1(\mathbf{p}_2,\,t-t')+g(x_1,\,x_2,\,t-t')]\\ &+\frac{1}{v}\int dx_3\theta_{13}F_1(\mathbf{p}_1,\,t-t')g(x_2,\,x_3,\,t-t')+\frac{1}{v}\int dx_3\theta_{23}F_1(\mathbf{p}_2,\,t-t')g(x_1,\,x_3,\,t-t')\\ &+\frac{1}{v}\int dx_3(\theta_{13}+\theta_{23})h(x_1,\,x_2,\,x_3,\,t-t')\Big\}\,.\end{aligned} \tag{8}$$

At this point we introduce the weak short-range potential and assume we can find a solution in the form

$$\begin{aligned}g(x_1,x_2,t)&=g^0(x_1,x_2,t)+\epsilon g^{(1)}(x_1,x_2,t)+\cdots\,,\\ h(x_1,x_2,x_3,t)&=h^0(x_1,x_2,x_3,t)+\epsilon h^{(1)}(x_1,x_2,x_3,t)+\cdots\,,\end{aligned} \tag{9}$$

etc., where ϵ is an expansion parameter that measures the strength of the potential (actually a measure of the ratio of the average potential to the average relative kinetic energy). For our purpose it will be sufficient to consider

probable form for F_s. This has been considered by Grad (Ref. 6) who has shown that most likely the F_s are uncorrelated.

[6] H. Grad, J. Chem. Phys. **33**, 1342 (1960).

$g^0(x_1,x_2,t_0)=h^0(x_1,x_2,x_3,t_0)=\cdots=0$. The zeroth- and first-order equations are then (dropping the ϵ notation)

$$g^0(x_1,x_2,t)=0\,,$$
$$g^{(1)}(x_1,x_2,t)=S_{-(t-t_0)}(x_1,x_2)g^{(1)}(x_1,x_2,t_0)+\int_0^{t-t_0}dt'S_{-t'}(x_1,x_2)\theta_{12}(x_1x_2)F_1(\mathbf{p}_1,\,t-t')F_1(\mathbf{p}_2,\,t-t')\,, \quad (10)$$
etc.

To this order, the equation for F_1 [Eq. (6a)] is

$$\frac{\partial F_1(\mathbf{p}_1,t)}{\partial t}=\frac{1}{v}\int dx_2\theta_{12}g^{(1)}(x_1,x_2,t)\,. \quad (11)$$

In Appendix A we prove that the set of Eqs. (10) and (11) are still reversible; the ϵ expansion has not destroyed the reversibility. This point is taken up again in Sec. IV.

III. RELAXATION OF THE CORRELATION FUNCTION

We now consider a special case, namely (taking $t_0=0$), $g^{(1)}(x_1,x_2,0)=0$.

(a) Consider first that $|\mathbf{q}_1-\mathbf{q}_2|<R$, where R is the range of the force. If we assume there exists a time τ, the "time of a collision," such that for essentially all relevant momenta

$$S_{-\tau}(x_1,x_2)\frac{\partial\varphi_{12}(|\mathbf{q}_1-\mathbf{q}_2|)}{\partial\mathbf{q}_1}=\partial\varphi_{12}\left(\left|\mathbf{q}_1-\mathbf{q}_2-\frac{(\mathbf{p}_1-\mathbf{p}_2)}{m}\tau\right|\right)\Big/\partial\mathbf{q}_1=0\,,$$

then Eq. (10) reduces, for $t\geqslant\tau$ to

$$g^{(1)}(x_1,x_2,t)=\int_0^{\tau}dt'S_{-t'}(x_1,x_2)\theta_{12}F_1(\mathbf{p}_1,\,t-t')F_1(\mathbf{p}_2,\,t-t')\,,\quad \text{for}\quad t\geqslant\tau; \quad (12)$$

and, from (11) we have

$$F_1(\mathbf{p}_i,\,t-t')=F_1(\mathbf{p}_i,t)+O(\tau/\mathcal{T})\ \text{for}\ 0\leqslant t'\leqslant\tau\,, \quad (13)$$

where $\mathcal{T}$ is the mean time between collisions.

To lowest order,

$$g_{\mathrm{FP}}^{(1)}(x_1,x_2,t)=\int_0^{\tau}dt'S_{-t'}(x_1,x_2)\theta_{12}F_1(\mathbf{p}_1,t)F_1(\mathbf{p}_2,t)\,,\quad \text{for}\quad t\geqslant\tau. \quad (14)$$

Therefore, to this order, the functional form proposed by Bogoliubov develops, for $|\mathbf{q}_1-\mathbf{q}_2|<R$, in a time τ from the initial time. The subscript F-P on $g^{(1)}$ indicates that this is the form of $g^{(1)}$ that together with Eq. (11) is the Fokker-Planck equation (or, as Bogoliubov calls it, the Landau equation). The Fokker-Planck equation is irreversible in the sense that it obeys an H theorem.[7]

(b) Consider $|\mathbf{q}_1-\mathbf{q}_2|>R$.

Suppose $\mathbf{p}_1$ and $\mathbf{p}_2$ are such that at no earlier time have the two points interacted, i.e., $|S_{-t}(x_1,x_2)\{\mathbf{q}_1-\mathbf{q}_2\}|>R$ for $0\leqslant t\leqslant\infty$; then $g^{(1)}(x_1,x_2,t)=0$ for all time.

If $\mathbf{p}_1$ and $\mathbf{p}_2$ are such that at an earlier time $\tau_0(x_1,x_2)$ the points are just starting to interact, i.e.,

$$|S_{-\tau_0}\{\mathbf{q}_1-\mathbf{q}_2\}|=R\,,$$

then Eq. (10) is

$$\begin{aligned}g^{(1)}(x_1,x_2,t)&=0\,,\quad t\leqslant\tau_0;\\&=\int_{\tau_0}^{t}dt'S_{-t'}(x_1x_2)\theta_{12}F_1(\mathbf{p}_1,\,t-t')F_1(\mathbf{p}_2,\,t-t')\,,\quad \tau_0\leqslant t\leqslant\tau_0+\tau;\\&=\int_{\tau_0}^{\tau_0+\tau}dt'S_{-t'}\theta_{12}F_1(\mathbf{p}_1,\,t-t')F_1(\mathbf{p}_2,\,t-t')\,,\quad t\geqslant\tau_0+\tau.\end{aligned} \quad (15)$$

The asymptotic form for $g^{(1)}$ is reached only after $t\geqslant\tau_0+\tau$ which can be (for given $\mathbf{p}_1$ and $\mathbf{p}_2$) arbitrarily large for points $\mathbf{q}_1$ and $\mathbf{q}_2$ sufficiently far apart. It is interesting to notice that the previous history of the system, in terms of F_1, is stored in the correlation function of distant points; for, at any time t, there are pairs of points $(\mathbf{q}_1,\mathbf{q}_2)$ such that the corresponding $g^{(1)}$ depends on the value of F_1 at any given time between zero and t.

The asymptotic form of (15) can be written as

$$\begin{aligned}g^{(1)}(x_1,x_2,t)&=\mathbf{J}(t-\tau_0)\cdot\mathbf{I}_{r_0}\,,\quad t\geqslant\tau_0+\tau\,,\\ \mathbf{J}(t)&=\left(\frac{\partial}{\partial\mathbf{p}_1}-\frac{\partial}{\partial\mathbf{p}_2}\right)F_1(\mathbf{p}_1,t)F_1(\mathbf{p}_2,t)\,,\\ \mathbf{I}_{r_0}&=\int_{\tau_0}^{\tau_0+\tau}dt'S_{-t'}(x_1,x_2)\frac{\partial\varphi_{12}}{\partial\mathbf{q}_1}\,,\end{aligned} \quad (16)$$

where we have again used Eq. (13) and, from the spherical symmetry of the force law and the fact that the collision is completed, $\mathbf{I}_{r_0}$ is in the direction of the distance of closest approach $\mathbf{r}_0$. Therefore, $g^{(1)}$ is nonzero if $\mathbf{J}$ has a component in the $\mathbf{r}_0$ direction. In equilibrium, $\mathbf{J}$ is in the direction of the relative momentum $\mathbf{P}=\mathbf{p}_2-\mathbf{p}_1$ which is normal to $\mathbf{r}_0$ so that $g^{(1)}=0$. We see then, in the nonequilibrium state, the range of $g^{(1)}$ can be arbitrarily large, but the range of $(\mathbf{p}_1,\mathbf{p}_2)$ which gives a nonzero value to $g^{(1)}$ goes down with increasing $|\mathbf{q}_1-\mathbf{q}_2|$. In Appendix B we show that the long range

[7] A. Lenard, Ann Phys. (N. Y.) 10, 390 (1960).

of $g^{(1)}$ does not cause the next approximation $g^{(2)}$ to become unbounded with time.

IV. THE REVERSE MOTION

In Sec. IIIa we considered the evolution of a system that at zero time was uncorrelated. In this section we shall describe the corresponding reverse motion. For this purpose we consider the evolution of a second system constructed at an arbitrary time $t_0>0$ that is identical to the first system but with all momenta reversed. This second system is initially correlated in a special way and it is this initial correlation which causes the reverse motion to be accomplished.

Consider again the initial condition $g^{(1)}(x_1,x_2,0)=0$. We have, from Eq. (10) with $t_0=0$

$$g^{(1)}(0|x_1,x_2,t)=\int_0^t dt' S_{-t'}(x_1,x_2)\theta_{12}F_1(0|\mathbf{p}_1,t-t')\times F_1(0|\mathbf{p}_2,t-t'),\quad(17)$$

where the zero preceding the vertical bar in $g^{(1)}$ and F_1 indicate the initial time was zero. In particular (suppressing $\mathbf{q}_1$, $\mathbf{q}_2$) we have

$$g^{(1)}(0|-\mathbf{p}_1,-\mathbf{p}_2,t)=\int_0^t dt' S_{-t'}(-\mathbf{p}_1,-\mathbf{p}_2)\theta_{12}(-\mathbf{p}_1,-\mathbf{p}_2)\times F_1(0|-\mathbf{p}_1,t-t')F_1(0|-\mathbf{p}_2,t-t').\quad(18)$$

At time t_0 start another system off with initial conditions

$$F_1(t_0|\mathbf{p}_1,t)|_{t=t_0}=F_1(0|-\mathbf{p}_1,t_0),\quad(19a)$$

$$g^{(1)}(t_0|\mathbf{p}_1,\mathbf{p}_2,t)|_{t=t_0}=g^{(1)}(0|-\mathbf{p}_1,-\mathbf{p}_2,t_0).\quad(19b)$$

For $t\geqslant t_0$ we have from Eq. (10)

$$g^{(1)}(t_0|\mathbf{p}_1,\mathbf{p}_2,t)=S_{-(t-t_0)}(\mathbf{p}_1,\mathbf{p}_2)g^{(1)}(t_0|\mathbf{p}_1,\mathbf{p}_2,t_0)+\int_0^{t-t_0} dt' S_{-t'}(\mathbf{p}_1,\mathbf{p}_2)\theta_{12}(\mathbf{p}_1,\mathbf{p}_2)\times F_1(t_0|\mathbf{p}_1,t-t')F_1(t_0|\mathbf{p}_2,t-t').\quad(20)$$

Using (19b) and (18) in (20) we have

$$g^{(1)}(t_0|\mathbf{p}_1,\mathbf{p}_2,t)=S_{-(t-t_0)}(\mathbf{p}_1,\mathbf{p}_2)\left\{\int_0^{t_0} dt' S_{-t'}(-\mathbf{p}_1,-\mathbf{p}_2)\theta_{12}(-\mathbf{p}_1,-\mathbf{p}_2)F_1(0|-\mathbf{p}_1,t_0-t')F_1(0|-\mathbf{p}_2,t_0-t')\right\}+\int_0^{t-t_0} dt' S_{-t'}(\mathbf{p}_1,\mathbf{p}_2)\theta_{12}(\mathbf{p}_1,\mathbf{p}_2)F_1(t_0|\mathbf{p}_1,t-t')F_1(t_0|\mathbf{p}_2,t-t').\quad(21)$$

In the first term in Eq. (21) we can combine the S operators

$$S_{-(t-t_0)}(\mathbf{p}_1,\mathbf{p}_2)S_{-t'}(-\mathbf{p}_1,-\mathbf{p}_2)=S_{-(t-t_0-t')}(\mathbf{p}_1,\mathbf{p}_2)=S_{-(t'+t_0-t)}(-\mathbf{p}_1,-\mathbf{p}_2).\quad(22)$$

Splitting the range of integration in the first integral in (21) into

$$(0,t-t_0)\quad\text{and}\quad(t-t_0,t_0)\quad\text{for}\quad t_0\leq t\leq 2t_0,$$

the first integral is

$$\left\{\int_0^{t-t_0} dt' S_{-(t-t_0-t')}(\mathbf{p}_1,\mathbf{p}_2)+\int_{t-t_0}^{t_0} dt' S_{-(t'+t_0-t)}(-\mathbf{p}_1,-\mathbf{p}_2)\right\}\theta_{12}F_1F_1.$$

Changing time variables, Eq. (21) becomes

$$\begin{aligned}g^{(1)}(t_0|\mathbf{p}_1,\mathbf{p}_2,t)=&\int_0^{t-t_0} dt' S_{-t'}(\mathbf{p}_1,\mathbf{p}_2)\theta_{12}(-\mathbf{p}_1,-\mathbf{p}_2)F_1(0|-\mathbf{p}_1,2t_0+t'-t)F_1(0|-\mathbf{p}_2,2t_0+t'-t)\\&+\int_0^{2t_0-t} dt' S_{-t'}(-\mathbf{p}_1,-\mathbf{p}_2)\theta_{12}(-\mathbf{p}_1,-\mathbf{p}_2)F_1(0|-\mathbf{p}_1,2t_0-t'-t)F_1(0|-\mathbf{p}_2,2t_0-t'-t)\\&+\int_0^{t-t_0} dt' S_{-t'}(\mathbf{p}_1,\mathbf{p}_2)\theta_{12}(\mathbf{p}_1,\mathbf{p}_2)F_1(t_0|\mathbf{p}_1,t-t')F_1(t_0|\mathbf{p}_2,t-t'),\quad\text{for}\quad t_0\leqslant t\leqslant 2t_0.\end{aligned}\quad(23)$$

From the general reversibility argument (Appendix A) we would expect

$$F_1(t_0|\mathbf{p}_1,t)=F_1(0|-\mathbf{p}_1,2t_0-t),\quad(24a)$$

$$g^{(1)}(t_0|\mathbf{p}_1,\mathbf{p}_2,t)=g^{(1)}(0|-\mathbf{p}_1,-\mathbf{p}_2,2t_0-t),\quad\text{for}\quad t_0\leq t\leq 2t_0,\quad(24b)$$

which satisfy the initial conditions (19a) and (19b). To show that this is the case, suppose (24a) is the solution of (23) and (11), then the first term in (23) cancels the last term and the remaining term is, by (18), $g^{(1)}(0|-\mathbf{p}_1, -\mathbf{p}_2, 2t_0-t)$ thus establishing (24b); and (24b) in (11) leads to (24a), i.e., Eq. (11) is

$$\frac{\partial F_1(t_0|\mathbf{p}_1,t)}{\partial t}=\frac{1}{v}\int dx_2\theta_{12}(\mathbf{p}_1,\mathbf{p}_2)g^{(1)}(t_0|\mathbf{p}_1,\mathbf{p}_2,t). \tag{25}$$

The right-hand side of (25) is

$$\frac{1}{v}\int dx_2\theta_{12}(\mathbf{p}_1,\mathbf{p}_2)g^{(1)}(0|-\mathbf{p}_1,-\mathbf{p}_2,2t_0-t)=-\frac{1}{v}\int dx_2\theta_{12}(-\mathbf{p}_1,-\mathbf{p}_2)g^{(1)}(0|-\mathbf{p}_1,-\mathbf{p}_2,2t_0-t) \tag{25a}$$

and the right side of (25a) is, by Eq. (11), $\partial F_1(0|-\mathbf{p}_1, 2t_0-t)/\partial t$; we have for $t_0\leq t\leq 2t_0$, $\partial F_1(t_0|\mathbf{p}_1,t)/\partial t=\partial F_1(0|-\mathbf{p}_1, 2t_0-t)/\partial t$, or $F_1(t_0|\mathbf{p}_1,t)-F_1(t_0|\mathbf{p}_1,t_0)=F_1(0|-\mathbf{p}_1, 2t_0-t)-F_1(0|-\mathbf{p}_1, t_0)$ and, with initial condition (19a), this is (24a).

Over the time interval $t_0\leq t\leq 2t_0$, the equation for $F_1(t_0|\mathbf{p}_1,t)$ can be obtained from (25) and (23). Equation (23) can be written, using (24a) and (13), as

$$\begin{aligned}g^{(1)}(t_0|\mathbf{p}_1,\mathbf{p}_2,t)&=\int_0^{2t_0-t}dt'S_{-t'}(-\mathbf{p}_1,-\mathbf{p}_2)\theta_{12}(-\mathbf{p}_1,-\mathbf{p}_2)F_1(0|-\mathbf{p}_1,2t_0-t'-t)F_1(0|-\mathbf{p}_2,2t_0-t'-t)\\&=-\int_0^{2t_0-t}dt'S_{-t'}(\mathbf{p}_1,\mathbf{p}_2)\theta_{12}(\mathbf{p}_1,\mathbf{p}_2)F_1(t_0|\mathbf{p}_1t)F_1(t_0|\mathbf{p}_2,t).\end{aligned} \tag{26}$$

Equation (26), together with (25), is the anti-Fokker-Planck equation, i.e., the collision term is the negative of the Fokker-Planck collision term. If we call $\mathbf{q}_1-\mathbf{q}_2=\mathbf{r}$ we have

$$\partial F_1(t_0|\mathbf{p}_1,t)/\partial t=-\frac{1}{v}\int d\mathbf{p}_2d\mathbf{r}\left[\frac{\partial\varphi(|\mathbf{r}|)}{\partial\mathbf{r}}\cdot\left\{\frac{\partial}{\partial\mathbf{p}_1}-\frac{\partial}{\partial\mathbf{p}_2}\right\}\right]\int_0^{2t_0-t}dt'\partial\varphi\left(\left|\mathbf{r}+\frac{(\mathbf{p}_1-\mathbf{p}_2)}{m}t'\right|\right)\Big/\partial\mathbf{r}\cdot\left\{\frac{\partial}{\partial\mathbf{p}_1}-\frac{\partial}{\partial\mathbf{p}_2}\right\}F_1(t_0|\mathbf{p}_1,t)F_1(t_0|\mathbf{p}_2,t).$$

Changing $\mathbf{r}\rightarrow-\mathbf{r}$

$$\frac{\partial F_1(t_0|\mathbf{p}_1,t)}{\partial t}=-\frac{1}{v}\int d\mathbf{p}_2d\mathbf{r}\left[\frac{\partial\varphi(|\mathbf{r}|)}{\partial\mathbf{r}}\cdot\left\{\frac{\partial}{\partial\mathbf{p}_1}-\frac{\partial}{\partial\mathbf{p}_2}\right\}\right]\int_0^{2t_0-t}dt'\partial\varphi\left(\left|\mathbf{r}-\frac{(\mathbf{p}_1-\mathbf{p}_2)}{m}t'\right|\right)\Big/\partial\mathbf{r}\cdot\left\{\frac{\partial}{\partial\mathbf{p}_1}-\frac{\partial}{\partial\mathbf{p}_2}\right\}F_1(t_0|\mathbf{p}_1,t)F_1(t_0|\mathbf{p}_2,t), \tag{27}$$

which is the anti-Fokker-Planck equation for $t_0\leqslant t\leqslant 2t_0-\tau$.

At time $t=2t_0$, from (24a) and (24b) we obtain

$$g^{(1)}(t_0|\mathbf{p}_1,\mathbf{p}_2,2t_0)=0, \tag{28a}$$

$$F_1(t_0|\mathbf{p}_1,2t_0)=F_1(0|-\mathbf{p}_1,0). \tag{28b}$$

The equation describing the motion for $t\geqslant 2t_0$ is then, from (11) and (10)

$$\frac{\partial F_1(2t_0|\mathbf{p}_1,t)}{\partial t}=\frac{1}{v}\int dx_2\theta_{12}g^{(1)}(2t_0|\mathbf{p}_1,\mathbf{p}_2,t), \tag{29a}$$

$$g^{(1)}(2t_0|\mathbf{p}_1,\mathbf{p}_2,t)=\int_0^{t-2t_0}dt'S_{-t'}(\mathbf{p}_1,\mathbf{p}_2)\theta_{12}(\mathbf{p}_1,\mathbf{p}_2)\times F_1(2t_0|\mathbf{p}_1,t)F_1(2t_0|\mathbf{p}_2,t), \tag{29b}$$

where

$$g^{(1)}(2t_0|\mathbf{p}_1,\mathbf{p}_2,2t_0)=0,\quad F_1(2t_0|\mathbf{p}_1,t)|_{t=2t_0}=F_1(0|-\mathbf{p}_1,0), \tag{29c}$$

and, therefore, after $t\geqslant 2t_0+\tau$ the equation for F_1 is again the Fokker-Planck equation and the system is again approaching equilibrium.

V. SUMMARY

From the BBKGY set of equations, we have derived an approximate set of equations for the weak force case, Eqs. (10) and (11); these have been shown to be reversible in Appendix A. In the special case that the initial $g^{(1)}=0$, the equation for F_1 evolves into the "irreversible" Fokker-Planck equation after a time τ (on the order of a time of a collision) and the system approaches equilibrium.

Suppose, on the other hand, the system is allowed to run for an arbitrary length of time t_0; then in order to describe the reverse motion, we consider a second system identical to the first at time t_0, but with all momenta reversed. The initial conditions on F_1 and $g^{(1)}$ for this second system are constructed from the F_1 and $g^{(1)}$ of the first system at t_0. The second system during the time interval $(t_0,2t_0)$ now performs exactly the reverse motion that the original system performed during the time $(0,t_0)$. The equation for F_1 for the second system during the time interval $(t_0, 2t_0-\tau)$ is the anti-Fokker-Planck equation and after the time $2t_0+\tau$ is the Fokker-Planck equation.

For the second system the dependence of $g^{(1)}$ on its initial value causes the reverse motion to be accomplished: "built into" the initial value of $g^{(1)}$ at pairs of points outside the range of the force is the earlier behavior of F_1 for the first system. The dependence of $g^{(1)}$ on its initial value would be missing if the momentum reversal were applied to the Fokker-Planck equation.

The final question of what to use in describing a given system is answered in the spirit of statistical mechanics by the argument that if all that is known initially about a system is F_1, then the most likely $g^{(1)}$ is zero and F_1 will most likely evolve according to the Fokker-Planck equation.[5]

APPENDIX A

Equations (10) and (11), with $t_0=0$, suppressing spatial coordinates in $g^{(1)}$ and S, are

$$\frac{\partial F_1(\mathbf{p}_1,t)}{\partial t}=\frac{1}{v}\int d\mathbf{q}_2 d\mathbf{p}_2 \frac{\partial\varphi_{12}}{\partial\mathbf{q}_1}\cdot\left(\frac{\partial}{\partial\mathbf{p}_1}-\frac{\partial}{\partial\mathbf{p}_2}\right)g^{(1)}(\mathbf{p}_1,\mathbf{p}_2,t), \quad \text{(A1)}$$

$$g^{(1)}(\mathbf{p}_1,\mathbf{p}_2,t) =S_{-t}(\mathbf{p}_1,\mathbf{p}_2)g^{(1)}(\mathbf{p}_1,\mathbf{p}_2,0) +\int_0^t dt' S_{-t'}(\mathbf{p}_1,\mathbf{p}_2)\frac{\partial\varphi_{12}}{\partial\mathbf{q}_1}\cdot\left(\frac{\partial}{\partial\mathbf{p}_1}-\frac{\partial}{\partial\mathbf{p}_2}\right) \times F_1(\mathbf{p}_1, t-t')F_1(\mathbf{p}_2, t-t'). \quad \text{(A2)}$$

Consider $\mathfrak{F}(\mathbf{p}_1,t)$ and $\mathfrak{G}(\mathbf{p}_1,\mathbf{p}_2,t)$ to be the solutions of (A1) and (A2) with initial conditions $\mathfrak{F}(\mathbf{p}_1,0)$ and $\mathfrak{G}(\mathbf{p}_1,\mathbf{p}_2,0)$. In Eqs. (A1) and (A2) change $\mathbf{p}_i\to-\mathbf{p}_i$ and $t\to-t$; then using the fact that $S_{-t}(\mathbf{p}_1,\mathbf{p}_2)=S_t(-\mathbf{p}_1,-\mathbf{p}_2)$ we have

$$\frac{\partial F_1(-\mathbf{p}_1,-t)}{\partial t}=\frac{1}{v}\int d\mathbf{q}_2 d\mathbf{p}_2 \frac{\partial\varphi_{12}}{\partial\mathbf{q}_1}\cdot\left(\frac{\partial}{\partial\mathbf{p}_1}-\frac{\partial}{\partial\mathbf{p}_2}\right) \times g^{(1)}(-\mathbf{p}_1,-\mathbf{p}_2,-t), \quad \text{(A3)}$$

$$g^{(1)}(-\mathbf{p}_1,-\mathbf{p}_2,-t) =S_{-t}(\mathbf{p}_1,\mathbf{p}_2)g^{(1)}(-\mathbf{p}_1,-\mathbf{p}_2,0) +\int_0^t dt' S_{-t'}(\mathbf{p}_1,\mathbf{p}_2)\frac{\partial\varphi_{12}}{\partial\mathbf{q}_1}\cdot\left(\frac{\partial}{\partial\mathbf{p}_1}-\frac{\partial}{\partial\mathbf{p}_2}\right) \times F_1(-\mathbf{p}_1,-t+t')F_1(-\mathbf{p}_2,-t+t'). \quad \text{(A4)}$$

Comparing Eqs. (A3) and (A4) with (A1) and (A2) we see that if we take as initial conditions in (A3) and (A4)

$$F_1(-\mathbf{p}_1,-t)|_{t=0}=\mathfrak{F}(\mathbf{p}_1,0),$$
$$g^{(1)}(-\mathbf{p}_1,-\mathbf{p}_2,-t)|_{t=0}=\mathfrak{G}(\mathbf{p}_1,\mathbf{p}_2,0),$$

then the solutions of (A3) and (A4) are

$$F_1(-\mathbf{p}_1,-t)=\mathfrak{F}(\mathbf{p}_1,t),$$
$$g^{(1)}(-\mathbf{p}_1,-\mathbf{p}_2,-t)=\mathfrak{G}(\mathbf{p}_1,\mathbf{p}_2,t),$$

or

$$F_1(\mathbf{p}_1,t)=\mathfrak{F}(-\mathbf{p}_1,-t),$$
$$g^{(1)}(\mathbf{p}_1,\mathbf{p}_2,t)=\mathfrak{G}(-\mathbf{p}_1,-\mathbf{p}_2,-t). \quad \text{(A5)}$$

Therefore, the approximation used to obtain Eqs. (A1) and (A2) have not destroyed the reversibility.

APPENDIX B

We show here that the long range of $g^{(1)}$ (see Sec. IIIb) does not cause the next approximation $g^{(2)}$ to become unbounded with increasing time. $g^{(2)}$ will contain a term

$$\frac{1}{v}\int_0^t dt' S_{-t'}(x_1,x_2)\int dx_3\theta_{13}F_1(\mathbf{p}_1,t-t')g^{(1)}(x_2,x_3,t-t')$$
$$=-\frac{1}{v}\int_0^t dt'\int d\mathbf{q}_3 d\mathbf{p}_3\frac{\partial\varphi_{13}}{\partial\mathbf{q}_1}(|\mathbf{q}_1'-\mathbf{q}_3|)\cdot\frac{\partial F_1(\mathbf{p}_1,t-t')}{\partial\mathbf{p}_1} \times g^{(1)}(x_2',x_3,t-t'), \quad \text{(B1)}$$

where

$$x_i'=S_{-t'}(x_1,x_2)x_i;\quad i=1,2.$$

Figure 1 shows a configuration at time t' where the integrand in (B1) is nonzero.

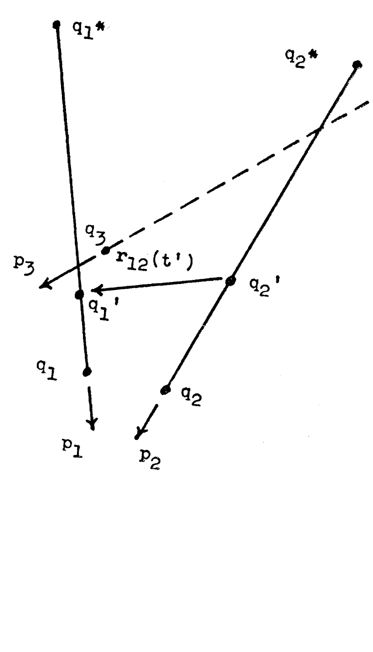

FIG. 1. An interacting configuration. (a) $\mathbf{q}_i^*=\mathbf{q}_i-\mathbf{p}_it/m$; $i=1, 2$. (b) $\mathbf{q}_3$ is within range of force of $\mathbf{q}_1'$ and (c) $\mathbf{p}_3$ is such that at an earlier time (but before particle 2 is at $\mathbf{q}_2^*$) particles 2 and 3 interact since $g^{(1)}\neq 0$ at that time.

In terms of the relative momentum $\mathbf{P}_{32}$; $\mathbf{P}_{32}$ must be within a solid angle $\pi R^2/|\mathbf{r}_{23}(t')|^2$ in the direction $\mathbf{r}_{23}(t')$, which at large distances can be replaced by $\pi R^2/|\mathbf{r}_{12}(t')|^2$, where $\mathbf{r}_{12}(t')=\mathbf{r}_{12}-\mathbf{P}_{12}t'/m$ and $\mathbf{r}_{12}=\mathbf{q}_1-\mathbf{q}_2$, $\mathbf{P}_{12}=\mathbf{p}_1-\mathbf{p}_2$.

In (B1) changing the momentum integration to $\mathbf{P}_{32}$ we have

$$\int_0^t dt' \int d\Omega_{P_{32}}\alpha\,, \qquad \alpha=-\frac{1}{v}\int d\mathbf{q}_3 dP_{32}P_{32}{}^2\frac{\partial\varphi_{13}}{\partial\mathbf{q}_1}\cdot\frac{\partial F_1}{\partial\mathbf{p}_1}g^{(1)}. \tag{B2}$$

To obtain the magnitude of (B2) we neglect the variation of α with time and treat it as constant with respect to the angles when it is nonzero. We then have

$$\alpha\int_0^t dt'\frac{\pi R^2}{|\mathbf{r}_{12}(t')|^2} =\frac{\alpha\pi R^2}{r_{12}(P_{12}/m)(1-\cos^2\theta)^{1/2}}\left\{\tan^{-1}\left[\frac{P_{12}t/mr_{12}-\cos\theta}{(1-\cos^2\theta)^{1/2}}\right]-\tan^{-1}\left[\frac{-\cos\theta}{(1-\cos^2\theta)^{1/2}}\right]\right\}, \tag{B3}$$

where θ is the angle between $\mathbf{r}_{12}$ and $\mathbf{P}_{12}$. Equation (B3) approaches a limit as $t\rightarrow\infty$, according to

$$\frac{\alpha\pi R^2}{r_{12}(P_{12}/m)(1-\cos^2\theta)^{1/2}}\left\{\frac{\pi}{2}-\tan^{-1}\left[\frac{-\cos\theta}{(1-\cos^2\theta)^{1/2}}\right]-\frac{(1-\cos^2\theta)^{1/2}}{P_{12}t/mr_{12}}\right\}. \tag{B4}$$

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Possibility of Synthesizing an Organic Superconductor*

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London's idea that superconductivity might occur in organic macromolecules is examined in the light of the BCS theory of superconductivity. It is shown that the criterion for the occurrance of such a state can be met in certain organic polymers. A particular example is considered in detail. From a realistic estimation of the matrix elements and density of states in this polymer it is concluded that superconductivity should occur even at temperatures well above room temperature. The physical reason for this remarkable high transition temperature is discussed. It is shown further that the superconducting state of these polymers should be distinguished by certain unique chemical properties which could have considerable biological significance.

I. INTRODUCTION

In the forward to Vol. 1 of his monographs on superfluids, F. London[1] questions whether a superfluid-like state might occur in certain macromolecules which play an important role in biochemical reactions. If this should be the case, an entirely new and important consideration would be added to the problem of understanding living systems. In view of the significance of such an effect, it appears appropriate at this time, when a theory of superconductivity, the Bardeen-Cooper-Schrieffer (BCS) theory[2] has been so remarkably successful in explaining much of the behavior of superconductors, to examine in the light of this whether or not a superconducting state might occur in certain macromolecules. In view of the extreme complexity of biological systems, it would be folly for a physicist to attempt to experiment in such an environment. Instead of attempting this, we shall tackle the problem on our own grounds. The BCS theory, while by no means complete and exact, has succeeded in providing a model with most of the essential features of a superconductor. In particular, it prescribes certain criteria for a system which, if satisfied, should lead to the superconducting state. Our approach is to consider how these criteria might be applied to the design of a particular organic molecule which, if its synthesis is possible, should show some of the essential features of a superconductor and, as we shall show, some remarkable chemical properties as well. One of the interesting features about the particular class of molecules we investigate in detail is that the molecules should be superconducting at room temperature and, indeed, to temperatures well above room temperatures. We can show on simple physical grounds why this is so and perhaps, with hindsight, why this was to be expected.

The idea of superconductivity in organic systems is not a new idea, however, there is a considerable amount

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[1] F. London, *Superfluids* (John Wiley & Sons, Inc., New York, 1950), Vol. 1.

[2] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).