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Approximate Eigenfunctions of the Liouville Operator in Classical Many-Body Systems

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A variational criterion is used to find approximate eigenfunctions and eigenvalues of the Liouville operator in classical many-body systems. The trial functions are taken to be sums over molecules of functions depending on the position and momentum of a single molecule. In a harmonic lattice, this approach leads to exact eigenfunctions and eigenvalues. In a fluid, the eigenvalue spectrum is continuous, and the eigenfunctions are related to those found by Van Kampen in his study of the linearized Vlasov equation for a plasma. The time dependence of the fluid current density is found by means of these eigenfunctions and eigenvalues. The results show persistent free-particle propagation and damped sound-wave propagation, with relative importance depending on the magnitude of the sound velocity.

INTRODUCTION AND SUMMARY

A CHARACTERISTIC feature of much recent work in statistical mechanics is the extensive use of collective variables in describing states of many-body systems. This is particularly true in solid-state physics and in superfluid physics.

Attempts to use the same ways of thinking about many-body systems, but in connection with *classical fluids*, have not met with much success. Perhaps this will turn out to be due to the inappropriateness of the approach; maybe there are no useful collective variables for classical fluids. But this failure may also be due, in part, to the inappropriateness of the kinds of collective variables that have been studied in this connection.

In this article, and in a later one, we describe some attempts to find good collective variables in classical many-body systems. The approach taken here is to use a variational criterion to find the "best" eigenfunctions of the classical Liouville operator (Poisson bracket operator), starting with various guesses as to the general structure of the eigenfunctions. In the present article we consider only eigenfunctions that are sums of single-particle functions. In a future article a different class of trial functions will be studied.

This approach resembles closely one that is familiar in quantum statistical mechanics: the "equation of motion method."[1] Use of a variational formulation, however, appears to have certain advantages over more conventional formulations of this method. One advantage lies in the great freedom of choice made available by searching for "best" eigenfunctions having various specified properties. Another advantage is due to the particular form of variational criterion used, which allows us to take into account many thermal equilibrium properties of the system under consideration.

The results obtained here are essentially as follows. In a perfect harmonic lattice, the "best" eigenfunctions having the form of sums of single-particle functions are the exact normal mode variables, and the corresponding eigenvalues are the exact lattice frequencies.

In a fluid (defined here is a translationally invariant many-body system) the eigenfunctions have a structure very much like those discussed by Van Kampen[2] and Case[3] in connection with the linearized Vlasov equation of plasma theory. An essential difference is that the interparticle potential, Coulomb in the plasma case, is replaced by the direct correlation function of the fluid. Instead of the plasma frequency, the frequency of a sound wave appears.

As in the Vlasov case, the eigenvalue spectrum is continuous. A phenomenon analogous to Landau damping occurs. That is, when the eigenfunctions are used to solve the initial value problem for the time dependence of the current density of the fluid, both persistent free-particle behavior and damped collective behavior are observed. The latter is controlled by the sound velocity of the fluid; the rate of damping becomes very small in the limit of high sound velocity, and very large in the limit of small sound velocity. Thus the free-particle behavior dominates at low density, and the collective behavior is of importance only at high density.

The article begins with a general discussion of the Liouville operator in classical mechanics, and its spectrum, along lines set forth many years ago by Koopman[4] and von Neumann.[5] Following this, a variational principle is demonstrated which leads to exact eigenfunctions and eigenvalues of the Liouville operator. Then the variational principle is applied to trial functions of the form of sums of single-particle functions, and an equation is derived for the "best" single-particle function. The solution of the equation is found, by inspection, for a perfect harmonic lattice. For a fluid, the equation is converted, by appropriate changes in variable and notation, into the linearized Vlasov equation, and solved by standard methods.[6]

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[1] This method is surveyed by D. Pines, in *The Many-Body Problem* (W. A. Benjamin, Inc., New York), 1961. See especially p. 44–48.

[2] N. G. Van Kampen, Physica **21**, 949 (1955); **23**, 641 (1957).

[3] K. M. Case, Ann. Phys. (N. Y.) **7**, 349 (1959).

[4] B. O. Koopman, Proc. Natl. Acad. Sci. U. S. **17**, 315 (1931).

[5] J. von Neumann, Ann. Math. **33**, 587, 789 (1932).

[6] We follow the treatment and notation of R. Balescu, *Statistical Mechanics of Charged Particles* (John Wiley & Sons, Ltd., London, 1963).

THE LIOUVILLE OPERATOR

We begin with a discussion of some general properties of the Liouville operator and its spectrum.

Consider a dynamical system with coordinates q_1, q_2, $\cdots$ and conjugate momenta p_1, p_2, $\cdots$. The sets of q's and p's will be denoted just by q and p. The Hamiltonian function is $H(p,q)$.

We define the Liouville operator by

$$Lf=-i\sum_{a}\left[\frac{\partial H}{\partial p_a}\frac{\partial f}{\partial q_a}-\frac{\partial H}{\partial q_a}\frac{\partial f}{\partial p_a}\right], \tag{1}$$

where $f(p,q)$ is an arbitrary function of the dynamical variables. This definition can also be written more concisely by means of the Poisson bracket operator $[f,H]$

$$Lf=-i[f,H]. \tag{2}$$

[Note that the definition contains a factor $i=\sqrt{-1}$. Originally the Liouville operator was introduced, by Koopman,[4] as the infinitesimal generator of a unitary transformation in the Hilbert space of measurable functions in phase space. This is the source of the factor i. For our purposes it is more natural and direct to define L as above, and to deduce from this the existence of the unitary operator.]

The most important property of the Liouville operator for the following discussion is its equivalence to the time derivative. The rate of change of some dynamical quantity $\alpha(p,q)$ is evidently given by

$$d\alpha/dt=iL\alpha. \tag{3}$$

On solving this equation symbolically as an initial-value problem, the value of α at time t is

$$\alpha(t)=\exp(itL)\alpha. \tag{4}$$

The exponential operator $\exp(itL)$ is the unitary operator introduced by Koopman. It may be called the time-displacement operator because of the way it shifts functions along trajectories in phase space.

Suppose now that α is an *eigenfunction* of L with the eigenvalue λ, or

$$L\alpha=\lambda\alpha. \tag{5}$$

Then the time dependence of α is known explicitly, and is

$$\alpha(t)=\exp(it\lambda)\alpha. \tag{6}$$

Constants of the motion are eigenfunctions with zero eigenvalue.

As was first shown by Koopman, the amplitude and phase of an eigenfunction have interesting properties of their own. The discussion of these properties starts with the observation that $\exp(itL)$ has a distributive effect on a function of a function

$$e^{itL}f(\alpha)=f(e^{itL}\alpha). \tag{7}$$

This can be verified, for example, by differentiation. Thus the effect of $\exp(itL)$ on the amplitude of a function is given by

$$e^{itL}|\alpha|=|e^{itL}\alpha|. \tag{8}$$

But if α is an eigenfunction with eigenvalue λ, then

$$e^{itL}|\alpha|=|e^{it\lambda}\alpha|=|\alpha|. \tag{9}$$

The amplitude of an eigenfunction is also an eigenfunction, and in particular it is a constant of the motion,

$$L|\alpha|=0. \tag{10}$$

The phase of the same eigenfunction, denoted here by θ,

$$\alpha=|\alpha|e^{i\theta} \tag{11}$$

obeys the equation

$$e^{i\theta(t)}=e^{itL}e^{i\theta}=e^{it\lambda}e^{i\theta}=e^{i(\theta+\lambda t)}. \tag{12}$$

The phase increases linearly with time, and is therefore an *angle variable*. The eigenvalue belonging to α is the frequency of the angle variable.

It is thus clear that eigenfunctions and eigenvalues of the Liouville operator can be constructed from the action-angle description of a system. The action variables are the constants of motion, and the amplitudes of the eigenfunctions are arbitrary functions of the actions. The phases of the eigenfunctions are just the angle variables.

In the special case of a system of coupled harmonic oscillators, the action variables are essentially the energies of individual normal modes of vibration, and the angle variables are the phases of the same normal modes.

By a similar argument, based on the identity

$$L\alpha\beta=\alpha L\beta+(L\alpha)\beta, \tag{13}$$

it is easy to see that any product of eigenfunctions is an eigenfunction; if

$$L\alpha=\lambda\alpha,\quad L\beta=\mu\beta, \tag{14}$$

then

$$L\alpha\beta=(\lambda+\mu)\alpha\beta, \tag{15}$$

so that the corresponding eigenvalue is the sum of the individual eigenvalues. This may be generalized immediately; any product of integral powers of eigenfunctions is an eigenfunction, and any linear combination (with integral coefficients) of eigenvalues is an eigenvalue. (The restriction to integral powers and integral coefficients is due to the requirement that eigenfunctions be single valued.)

What does this tell us about the nature of the spectrum of the classical Liouville operator? Barring accidental cases, where all eigenvalues are commensurable, the spectrum is at least countably infinite and unbounded. For a harmonic lattice, the spectrum is a point spectrum, densely distributed over the entire real axis in the limit of a very large lattice.

The harmonic case, however, appears to be unique. In general the spectrum of L is continuous. This may be seen from the action-angle picture. Suppose that the action variables are $J_1, J_2, \cdots$. Then the eigenvalues are the frequencies of motion,

$$\nu_a(J) = \partial H(J)/\partial J_\alpha, \quad (a=1, 2, \cdots), \tag{16}$$

and their linear combinations. But in general the energy is not a linear function of J, so that $\nu(J)$ varies with J. (For example, the frequency of the anharmonic oscillator governed by the Hamiltonian $\frac{1}{2}p^2+q^4$ is proportional to $J^{1/3}$.) By varying J continuously, the frequency ν varies continuously, and so the spectrum is continuous. The only exception is when $\nu(J)$ is actually independent of J. This can happen only for harmonic oscillators.

It should be noted that the spectrum with respect to constraints may have an entirely different character than the total spectrum. For example, if we consider only systems with specified actions J, then the spectrum is discrete. Normally, however, in statistical mechanics we do not have so much information under control; if only the total energy is specified, then the spectrum is generally expected to be continuous.

A VARIATIONAL PRINCIPLE

As is well known, eigenvalue problems can be formulated by means of variational principles. In the present instance, the variational integral is constructed as follows.

First we introduce a weighting function. Let $f(p,q)$ be some time-invariant distribution function in phase space, so that

$$Lf(p,q) = 0. \tag{17}$$

For convenience we normalize $f(p,q)$ to unity,

$$\int\int dpdqf(p,q) = 1. \tag{18}$$

While in general $f(p,q)$ may be any measurable function of known constants of the motion, we shall always take it to be the canonical ensemble distribution function for a system in thermal equilibrium.

Average values taken with respect to $f(p,q)$ will be denoted by angular brackets,

$$\langle\alpha\rangle \equiv \int\int dpdqf(p,q)\alpha(p,q). \tag{19}$$

Now we introduce a trial function $\psi(p,q)$, and its complex conjugate $\psi^*(p,q)$, and we form the ratio

$$[\lambda] = \langle\psi^* L\psi\rangle/\langle\psi^*\psi\rangle. \tag{20}$$

The requirement that $[\lambda]$ be stationary with respect to small variations in ψ and ψ^*,

$$\delta[\lambda] = 0, \tag{21}$$

leads directly to the eigenvalue equations for ψ and ψ^*,

$$\begin{aligned} L\psi &= \lambda\psi, \\ L\psi^* &= \lambda\psi^*. \end{aligned} \tag{22}$$

Because L is Hermitian, its eigenvalues are real.

Note that ψ itself does not have to be integrable over phase space. Convergence of integrals is taken care of by the weighting function $f(p,q)$.

The chosen distribution function $f(p,q)$ drops out of the exact eigenvalue equation, simply because of its time invariance,

$$L(f\psi) = fL\psi. \tag{23}$$

If, however, we choose trial functions that cannot lead to exact eigenfunctions because they have the wrong structure, then the resulting "best" trial functions will depend on the choice of $f(p,q)$. An example will be discussed later.

EIGENVALUE EQUATION FOR SINGLE-PARTICLE TRIAL FUNCTIONS

For the rest of this article we consider a system of N identical molecules contained in a volume V, having positions $\mathbf{R}_1, \mathbf{R}_2, \cdots$ and momenta $\mathbf{p}_1, \mathbf{p}_2, \cdots$. (These quantities all refer to the center of mass of each molecule. Internal molecular structure is not of interest in the present calculation.) For convenience the variables $\mathbf{R}_j$, $\mathbf{p}_j$ will often be denoted by (j).

The trial functions to be used here have the form of a sum over molecules of an arbitrary function of the position and momentum of an individual molecule,

$$\Psi = \sum_j \psi(\mathbf{R}_j,\mathbf{p}_j) = \sum_j \psi(j). \tag{24}$$

The denominator in Eq. (20), by virtue of the symmetry between identical molecules, takes on the form

$$\langle\Psi^*\Psi\rangle = N\langle\psi^*(1)\psi(1)\rangle + N(N-1)\langle\psi^*(2)\psi(1)\rangle. \tag{25}$$

The averages can be written more explicitly using the single-particle distribution function $f(1)$, defined by

$$f(1) = \int d(2)\cdots d(N)f(1,2,\cdots N) \tag{26}$$

and the two-particle distribution function $f(1,2)$ defined by

$$f(1,2) = \int d(3)\cdots d(N)f(1,2,\cdots N). \tag{27}$$

Then the denominator is

$$\langle\Psi^*\Psi\rangle = N\int d(1)f(1)\psi^*(1)\psi(1) + N(N-1)\int d(1)\int d(2)f(1,2)\psi^*(2)\psi(1). \tag{28}$$

The numerator in Eq. (20) is

$$\langle\Psi^* L\Psi\rangle = N\langle\Psi^* L\psi(1)\rangle. \tag{29}$$

The Liouville operator is

$$L=-i\sum_j \frac{\mathbf{p}_j}{m}\cdot\frac{\partial}{\partial\mathbf{R}_j}-i\sum_j \mathbf{F}_j\cdot\frac{\partial}{\partial\mathbf{p}_j}, \tag{30}$$

where $\mathbf{F}_j$ is the total force on the jth molecule. Consequently, when L operates on $\psi(1)$, we get only the contribution from the first molecule,

$$L\psi(1)=-i\frac{\mathbf{p}_1}{m}\cdot\frac{\partial\psi(1)}{\partial\mathbf{R}_1}-i\mathbf{F}_1\cdot\frac{\partial\psi(1)}{\partial\mathbf{p}_1}. \tag{31}$$

On integration by parts, taking advantage of the invariant character of $f(1,2,3,\cdots,N)$, we find that the cross terms connecting molecules j and k all vanish, leaving

$$\langle\Psi^* L\Psi\rangle = N\left\langle \psi^*(1)\left[-i\frac{\mathbf{p}_1}{m}\cdot\frac{\partial}{\partial\mathbf{R}_1}-i\mathbf{F}_1\cdot\frac{\partial}{\partial\mathbf{p}_1}\right]\psi(1)\right\rangle. \tag{32}$$

We define the average force on a particular molecule by

$$\langle\mathbf{F}_1;1\rangle=\int d(2)\cdots d(N)f(1,2,\cdots N)\mathbf{F}_1/f(1). \tag{33}$$

Thus the numerator in Eq. (20) is

$$N\int d(1)f(1)\psi^*(1)\left[-i\frac{\mathbf{p}_1}{m}\cdot\frac{\partial}{\partial\mathbf{R}_1}-i\langle\mathbf{F}_1;1\rangle\cdot\frac{\partial}{\partial\mathbf{p}_1}\right]\psi(1). \tag{34}$$

When the numerator and denominator are combined, and the variation with respect to ψ^* is taken, the resulting eigenvalue equation for ψ is

$$\left[-i\frac{\mathbf{p}_1}{m}\cdot\frac{\partial}{\partial\mathbf{R}_1}-i\langle\mathbf{F}_1;1\rangle\cdot\frac{\partial}{\partial\mathbf{p}_1}\right]\psi(1) =\lambda\left[\psi(1)+(N-1)\int d(2)\frac{f(1,2)}{f(1)}\psi(2)\right]. \tag{35}$$

This is the fundamental equation of the present article. Its solution is described in the following sections.

Harmonic Lattice

The normal-mode variables of a harmonic lattice (with one molecule per unit cell) have just the same structure as our assumed trial function (24); so we expect that the preceding equation for the "best" trial function is obeyed by these normal-mode variables. This is demonstrated now.

Because of lattice symmetry, the most general solution of (35) has the form of a Bloch wave,

$$\psi(\mathbf{R},\mathbf{p})=e^{i\mathbf{K}\cdot\mathbf{R}^0}\phi(\mathbf{R}-\mathbf{R}^0,\,\mathbf{p}), \tag{36}$$

where $\mathbf{K}$ is a vector of the reciprocal lattice, $\mathbf{R}^0$ is the equilibrium position of a molecule in its unit cell, and ϕ has the periodicity of the lattice. The eigenvalue equation is then transformed to

$$\left[-i\frac{\mathbf{p}_1}{m}\cdot\frac{\partial}{\partial\mathbf{R}_1}-i\langle\mathbf{F}_1;1\rangle\cdot\frac{\partial}{\partial\mathbf{p}_1}\right]\phi(1) =\lambda\phi(1)+\lambda\int d(2)\frac{f(1,2)}{f(1)}\phi(2)e^{i\mathbf{K}\cdot(\mathbf{R}_2{}^0-\mathbf{R}_1{}^0)}. \tag{37}$$

In the canonical ensemble, the reduced distribution functions may be expressed in terms of a Boltzmann distribution of momentum,

$$\varphi_B(\mathbf{p})=(2\pi mkT)^{-3/2}\exp(-p^2/2mkT) \tag{38}$$

and the one- and two-particle space densities

$$\begin{aligned}\rho^{(1)}(\mathbf{R}_1)&=f(1)/\varphi_B(\mathbf{p}_1),\\ \rho^{(2)}(\mathbf{R}_1,\mathbf{R}_2)&=f(1,2)/\varphi_B(\mathbf{p}_1)\varphi_B(\mathbf{p}_2).\end{aligned} \tag{39}$$

Thus the integrand in (37) contains

$$f(1,2)/f(1)=\varphi_B(\mathbf{p}_2)\rho^{(2)}(\mathbf{R}_1,\mathbf{R}_2)/\rho^{(1)}(\mathbf{R}_1). \tag{40}$$

The integration over position $\mathbf{R}_2$ may be decomposed into a sum over unit cells (excluding the cell $j=1$, because we are dealing here with the *pair* function of distinct molecules), and an integration over a given unit cell. The trial function has the symmetry of the lattice, and is independent of the identity of any given cell. Then the right-hand side of (37) becomes

$$\lambda\phi(1)+\lambda\sum_{j\neq 1}e^{i\mathbf{K}\cdot(\mathbf{R}_j{}^0-\mathbf{R}_1{}^0)} \times\int_{\text{cell}}d\mathbf{r}\int d\mathbf{p}_2\varphi_B(\mathbf{p}_2)\frac{\rho^{(2)}(\mathbf{R}_1,\mathbf{R}_j{}^0+\mathbf{r})}{\rho^{(1)}(\mathbf{R}_1)}\phi(\mathbf{r},\mathbf{p}_2). \tag{41}$$

In a canonical ensemble, the mean force $\langle\mathbf{F}_1;1\rangle$ can be obtained from the familiar identity

$$\langle\mathbf{F}_1;1\rangle=kT\frac{\partial}{\partial\mathbf{R}_1}\ln\rho^{(1)}(\mathbf{R}_1). \tag{42}$$

(It should be recalled that the present treatment is based on classical mechanics.)

The space densities $\rho^{(1)}$ and $\rho^{(2)}$ may be found easily by direct integration, because the potential energy is quadratic and the complete N molecule distribution function is Gaussian in its arguments. In fact, both $\rho^{(1)}$ and $\rho^{(2)}$ are themselves Gaussian in their arguments, so that it is sufficient to find their first and second moments. For example, the one-particle density is

$$\rho^{(1)}(\mathbf{R}_1)\sim\exp-\tfrac{1}{2}(\mathbf{R}_1-\mathbf{R}_1{}^0)\cdot\mathbf{g}\cdot(\mathbf{R}_1-\mathbf{R}_1{}^0) \tag{43}$$

aside from normalization. The matrix $\mathbf{g}$ is connected with the second moment of displacements within a unit cell

$$\mathbf{g}^{-1}=\langle(\mathbf{R}_1-\mathbf{R}_1{}^0)(\mathbf{R}_1-\mathbf{R}_1{}^0)\rangle. \tag{44}$$

The corresponding mean force is linear and displacements

$$\langle\mathbf{F}_1;1\rangle=-kT\mathbf{g}\cdot(\mathbf{R}_1-\mathbf{R}_1{}^0) \tag{45}$$

and the left-hand side of (37) is

$$\left[-i\frac{\mathbf{p}_1}{m}\cdot\frac{\partial}{\partial\mathbf{R}_1}+ikT(\mathbf{R}_1-\mathbf{R}_1{}^0)\cdot\mathbf{g}\cdot\frac{\partial}{\partial\mathbf{p}_1}\right]\phi(1). \tag{46}$$

This looks just like the Liouville operator for a one-particle system in a harmonic well, and suggests that the general solution of (37) will have the form

$$\phi=\mathbf{a}\cdot(\mathbf{R}-\mathbf{R}^0)+\mathbf{b}\cdot\mathbf{p}. \tag{47}$$

On substitution into (37), the left-hand side becomes

$$-i(\mathbf{p}_1/m)\cdot\mathbf{a}+ikT(\mathbf{R}_1-\mathbf{R}_1{}^0)\cdot\mathbf{g}\cdot\mathbf{b}. \tag{48}$$

If the same substitution is made in the right-hand side of (37), we get

$$\lambda\mathbf{a}\cdot(\mathbf{R}_1-\mathbf{R}_1{}^0)+\lambda\mathbf{b}\cdot\mathbf{p}_1$$
$$+\lambda\sum_{j\neq1}e^{i\mathbf{K}\cdot(\mathbf{R}_j{}^0-\mathbf{R}_1{}^0)}\int_{\text{cell}}d\mathbf{r}\frac{\rho^{(2)}(\mathbf{R}_1,\mathbf{R}_j{}^0+\mathbf{r})}{\rho^{(1)}(\mathbf{R}_1)}\mathbf{a}\cdot\mathbf{r}. \tag{49}$$

The momentum contribution to ϕ drops out of the integral by symmetry.

Because of the Gaussian character of $\rho^{(1)}$ and $\rho^{(2)}$, the integral over $\mathbf{r}$ gives a quantity linear in $\mathbf{R}_1-\mathbf{R}_1{}^0$. When this is worked out, the result is

$$\mathbf{a}\cdot\langle(\mathbf{R}_j-\mathbf{R}_j{}^0)(\mathbf{R}_1-\mathbf{R}_1{}^0)\rangle\cdot\mathbf{g}\cdot(\mathbf{R}_1-\mathbf{R}_1{}^0) \tag{50}$$

which contains the correlation of displacements in the first and jth cells.

By equating coefficients of momentum and displacement, which are linearly independent variables, we obtain from the preceding arguments a pair of equations for $\mathbf{a}$ and $\mathbf{b}$,

$$-(i/m)\mathbf{a}=\lambda\mathbf{b};$$
$$ikT\mathbf{g}\cdot\mathbf{b}=\lambda\mathbf{a}+\lambda\sum_{j\neq1}e^{i\mathbf{K}\cdot(\mathbf{R}_j{}^0-\mathbf{R}_1{}^0)} \tag{51}$$
$$\times\mathbf{a}\cdot\langle(\mathbf{R}_j-\mathbf{R}_j{}^0)(\mathbf{R}_1-\mathbf{R}_1{}^0)\rangle\cdot\mathbf{g}.$$

The quantity $\mathbf{b}$ may be eliminated easily, leaving

$$(kT/m\lambda^2)\mathbf{a}$$
$$=\mathbf{a}\cdot\textstyle\sum_j e^{i\mathbf{K}\cdot(\mathbf{R}_j{}^0-\mathbf{R}_1{}^0)}\langle(\mathbf{R}_j-\mathbf{R}_j{}^0)(\mathbf{R}_1-\mathbf{R}_1{}^0)\rangle. \tag{52}$$

Note that the sum over lattice sites now includes all sites.

To complete the calculation, we express the displacements in terms of normal coordinates, and find their second moments from equipartition. The argument is straightforward but a little tedious; to save space, we give the details only for a one-dimensional lattice. The three-dimensional case is handled in exactly the same way.

If Q_K is the Kth normal-mode coordinate, then the displacements are given by

$$R_j-R_j{}^0=(1/\sqrt{N})\textstyle\sum_K e^{iKR_j{}^0}Q_K. \tag{53}$$

The sum over j in (52) reduces easily, and the eigenvalue equation becomes

$$(kT/m\lambda^2)a=a\langle Q_K{}^*Q_K\rangle. \tag{54}$$

By equipartition, the second moment of Q_K is related to the frequency ω_K of the Kth mode by

$$\langle Q_K{}^*Q_K\rangle=kT/m\omega_K{}^2. \tag{55}$$

Then the nontrivial solution of (54) is

$$\lambda^2=\omega_K{}^2 \tag{56}$$

which shows that the present variational method leads to the exact eigenvalues of the system.

The eigenfunctions can be found from (51). We choose

$$a=(i\omega_K/\sqrt{N}). \tag{57}$$

Then the resulting eigenfunctions are

$$\Psi=\dot{Q}_K\pm i\omega_K Q_K. \tag{58}$$

The "best" eigenfunctions are clearly the exact eigenfunctions of the Liouville operator in the present example.

APPROXIMATE EIGENFUNCTIONS FOR FLUIDS

We now describe the solution of the fundamental eigenvalue equation (35) for a fluid phase.

In a fluid, the one-particle space density is independent of position,

$$\rho^{(1)}(\mathbf{R})=1/V \tag{59}$$

and the two-particle space density is proportional to the radial distribution function $g(r)$,

$$\rho^{(2)}(\mathbf{R}_1,\mathbf{R}_2)=(1/V^2)g(\mathbf{R}_1-\mathbf{R}_2). \tag{60}$$

As indicated by Eq. (42), the mean force $\langle\mathbf{F}_1;1\rangle$ on a particle vanishes,

$$\langle\mathbf{F}_1;1\rangle\sim\partial\rho^{(1)}/\partial\mathbf{R}_1=0. \tag{61}$$

Thus the eigenvalue equation reduces to

$$-i\frac{\mathbf{p}_1}{m}\cdot\frac{\partial\psi}{\partial\mathbf{R}_1}=\lambda\psi+\lambda\frac{N}{V}\int d\mathbf{p}_2\int d\mathbf{R}_2\varphi_B(\mathbf{p}_2)$$
$$\times g(\mathbf{R}_1-\mathbf{R}_2)\psi(\mathbf{R}_2,\mathbf{p}_2). \tag{62}$$

(The difference between $N-1$ and N is negligible in a large system.)

Because of translational invariance, the eigenvalue equation can always be solved by functions of the form

$$\psi(\mathbf{R},\mathbf{p})=e^{i\mathbf{k}\cdot\mathbf{R}}\gamma(\mathbf{p}), \tag{63}$$

where $\mathbf{k}$ is an arbitrary vector. When this is substituted in (62), we obtain

$$(\mathbf{k}\cdot\mathbf{p}_1/m)\gamma(\mathbf{p}_1)=\lambda\gamma(\mathbf{p}_1)+\lambda\frac{N}{V}\int d\mathbf{R}_2 g(\mathbf{R}_2-\mathbf{R}_1)e^{i\mathbf{k}\cdot(\mathbf{R}_2-\mathbf{R}_1)}\times\int d\mathbf{p}_2\varphi_B(\mathbf{p}_2)\gamma(\mathbf{p}_2). \tag{64}$$

Let us define the Fourier transform of the radial distribution function by

$$G(\mathbf{k})=\int d\mathbf{R}_{21}g(\mathbf{R}_{21})e^{i\mathbf{k}\cdot\mathbf{R}_{21}}. \tag{65}$$

Then the eigenvalue equation becomes

$$(\mathbf{k}\cdot\mathbf{p}_1/m)\gamma(\mathbf{p}_1)=\lambda\gamma(\mathbf{p}_1)+\lambda\frac{N}{V}G(\mathbf{k})\int d\mathbf{p}_2\varphi_B(\mathbf{p}_2)\gamma(\mathbf{p}_2). \tag{66}$$

Note that the only property of the material entering into this equation is its radial distribution function. This quantity depends on the initial choice of weighting function; we picked the canonical-ensemble distribution function. By changing the weighting function, we change $g(r)$, and thereby change the resulting approximate eigenfunctions. [It should be remembered, however, that $g(r)$ is rather insensitive to the choice of ensemble, and does not differ appreciably, for example, between a microcanonical ensemble for a given energy, and a canonical ensemble that gives the same mean energy.]

By a suitable change in variables, Eq. (66) can be made to resemble the linearized Vlasov equation. We shall use essentially the same notation as in Balescu's book.[6]

First, for simplicity, we set $m=1$, and we replace the momentum $\mathbf{p}$ by the velocity $\mathbf{v}$. The mean density N/V will be denoted by n. The decisive change is to replace γ by the new function χ, defined as

$$\chi\equiv\varphi_B(\mathbf{v})\gamma(\mathbf{v})+nG(\mathbf{k})\varphi_B(\mathbf{v})\int d\mathbf{v}'\varphi_B(\mathbf{v}')\gamma(\mathbf{v}'). \tag{67}$$

The inverse transformation can be obtained easily with the aid of the identity (verifiable directly by integration)

$$\int d\mathbf{v}\chi(\mathbf{v})=[1+nG(\mathbf{k})]\int d\mathbf{v}\varphi_B(\mathbf{v})\gamma(\mathbf{v}). \tag{68}$$

Then the inverse transformation is

$$\gamma(\mathbf{v})=\frac{\chi(\mathbf{v})}{\varphi_B(\mathbf{v})}-\frac{nG(\mathbf{k})}{1+nG(\mathbf{k})}\int d\mathbf{v}'\chi(\mathbf{v}'). \tag{69}$$

When the indicated changes are made in (66), we obtain

$$\mathbf{k}\cdot\mathbf{v}\chi(\mathbf{v})-\frac{nG(\mathbf{k})}{1+nG(\mathbf{k})}\mathbf{k}\cdot\mathbf{v}\varphi_B(\mathbf{v})\int d\mathbf{v}'\chi(\mathbf{v}')=\lambda\chi(\mathbf{v}). \tag{70}$$

Because φ_B is the Boltzmann distribution, so that

$$-\mathbf{k}\cdot\mathbf{v}\varphi_B=k_BT\mathbf{k}\cdot\partial\varphi_B/\partial\mathbf{v}, \tag{71}$$

we may rewrite (70) as

$$\mathbf{k}\cdot\mathbf{v}\chi+k_BT\frac{nG(\mathbf{k})}{1+nG(\mathbf{k})}\mathbf{k}\cdot\frac{\partial}{\partial\mathbf{v}}\varphi_B\int d\mathbf{v}'\chi(\mathbf{v}')=\lambda\chi(v). \tag{72}$$

(To avoid confusion in notation, we denote Boltzmann's constant by k_B instead of the conventional k.) Now we introduce the abbreviation

$$\nu_p^2=-k_BTnG(\mathbf{k})/[1+nG(\mathbf{k})], \tag{73}$$

and the above equation becomes

$$\mathbf{k}\cdot\mathbf{v}\chi-\nu_p^2\mathbf{k}\cdot\frac{\partial\varphi_B}{\partial\mathbf{v}}\int d\mathbf{v}'\chi(\mathbf{v}')=\lambda\chi. \tag{74}$$

This has exactly the same structure as the linearized Vlasov equation.

In plasma problems, the quantity ν_p^2 takes the value

$$\nu_p^2=\omega_p^2/k^2, \tag{75}$$

where ω_p is the plasma frequency. This is actually a special case of (73), as can be seen by using the Debye-Huckel radial distribution function for $G(\mathbf{k})$.

In the general theory of the Vlasov equation for an arbitrary system, as set forth by Balescu, the parameter ν_p^2 corresponds to the Fourier transform $U(\mathbf{k})$ of the intermolecular potential,

$$\nu_p^2=nU(\mathbf{k}). \tag{76}$$

Equation (75) follows from this in the Coulomb case.

In the present theory, the parameter ν_p^2 is proportional to the Fourier transform $C(\mathbf{k})$ of the direct correlation function,

$$\nu_p^2=-nk_BTC(\mathbf{k}), \tag{77}$$

where

$$C(\mathbf{k})=G(\mathbf{k})/[1+nG(\mathbf{k})]. \tag{78}$$

Thus we may introduce an effective potential $U_{\text{eff}}(\mathbf{k})$,

$$U_{\text{eff}}=-k_BTC. \tag{79}$$

It should be noted that this effective potential has a definite physical and mathematical significance even for hard-sphere systems, where the Fourier transform $U(\mathbf{k})$ of the actual potential does not exist.

The parameter ν_p^2 may be related also to a sound velocity. We observe first that the Fourier transform of the radial distribution function can be expressed in terms of a $\mathbf{k}$-dependent compressibility $\kappa(\mathbf{k})$ according to

$$1+nG(\mathbf{k})=nk_BT\kappa(\mathbf{k}). \tag{80}$$

The $\mathbf{k}$-dependent isothermal sound velocity $B(\mathbf{k})$ is related to the compressibility by

$$B^2(\mathbf{k})=1/M\kappa(\mathbf{k}), \tag{81}$$

so that

$$\nu_p^2=B^2(\mathbf{k})-k_BT. \tag{82}$$

In low-density gases, $B(\mathbf{k})$ is very close to k_BT, and ν_p is very small. In dense systems, on the other hand, the sound velocity is large and ν_p is large.

The distinction between an ordinary fluid and a plasma lies in the behavior of ν_p^2 or $B^2(\mathbf{k})$ for small $\mathbf{k}$. In an ordinary fluid these quantities approach finite limits, while in a plasma they diverge as $1/k^2$.

Van Kampen showed how to solve the linearized Vlasov equation as an eigenvalue problem. His results (and their extension by Case) are directly applicable here. The eigenvalues are real and form a continuous spectrum: Every λ is an eigenvalue. The functions associated with any given λ are singular, i.e., they are distributions in the sense of the theory of generalized functions. They are given explicitly in Chap. 5 of Balescu's book. We shall not write them down here. Knowing χ, however, we can form the desired eigenfunctions of the Liouville operator by means of Eqs. (63) and (69). (*Note added in proof.* The eigenfunctions γ are given explicitly at the end of this article.)

AN INITIAL-VALUE PROBLEM

Just as in plasma theory, the eigenfunctions that we have found here are not particularly informative. One can get a better physical picture by using them to solve an initial-value problem. An example will be given now.

The problem to be considered is to find the time evolution of the quantity that, at time $t=0$, has the form

$$\Psi=\textstyle\sum_j e^{i\mathbf{k}\cdot\mathbf{R}_j}\mathbf{p}_j\cdot\mathbf{k}/|k| \tag{83}$$

or

$$\gamma(\mathbf{p})=\mathbf{p}\cdot\mathbf{k}/|k|. \tag{84}$$

This is in fact the longitudinal current density of the fluid.

The calculation involves the following steps. First, γ is converted to χ by means of the transformation given in Eq. (67). Next, this χ is expanded in a series of Van Kampen–Case eigenfunctions. Next, the time dependence of each individual eigenfunction is inserted. Finally, the series is resummed. A procedure for accomplishing this is given in Chap. 5 of Balescu's book; we shall omit the details here.

To conform to Balescu's notation, we replace λ by

$$\lambda=k\nu, \tag{85}$$

we use v for the longitudinal part of $\mathbf{v}$ (the transverse parts being of no concern in this calculation), and we use $\bar{\varphi}_B$ for the Boltzmann distribution in the single component v.

The analog of the plasma dielectric constant is

$$\begin{aligned}\epsilon_\pm(\nu)&=\epsilon_1(\nu)\mp i\epsilon_2(\nu),\\ \epsilon_1(\nu)&=1+\nu_p^2\,\mathrm{P}\int dv\ \bar{\varphi}_B'(v)\frac{1}{v-\nu},\\ \epsilon_2(\nu)&=\pi\nu_p^2\,\bar{\varphi}_B'(\nu),\end{aligned} \tag{86}$$

where P means the principal part.

Then Balescu's prescription for solving an initial-value problem leads to the result

$$\gamma(t)=[v/\epsilon_+(v)]e^{-ikvt}-\frac{1}{\pi}\oint d\nu\,\frac{\nu}{\nu-v}\,\frac{\epsilon_2(\nu)}{\epsilon_+(\nu)\epsilon_-(\nu)}e^{-ik\nu t}, \tag{87}$$

where the contour for the ν integration lies *below* the real axis, and surrounds all singularities in the lower half-plane. (This solution holds for positive times only.)

We evaluate the contour integral by residue theory. The singularities in the lower half-plane (excluding the real axis) come only from the zeros ν_r of the dielectric constant ϵ_+,

$$\epsilon_+(\nu_r)=0,\quad r=1,2,\cdots. \tag{88}$$

By residue theory, the result is

$$\gamma(t)=[v/\epsilon_+(v)]e^{-ikvt}-2i\sum_r\frac{\nu_r}{\nu_r-v}\,\frac{\epsilon_2(\nu_r)}{\epsilon_-(\nu_r)}\,\frac{1}{(d\epsilon_+/d\nu)_r}e^{-ik\nu_r t}. \tag{89}$$

The first term in $\gamma(t)$ persists for all times, and the time dependence is just as if the molecule were moving freely. The remaining terms in $\gamma(t)$ are all damped in time, because all the zeros ν_r have negative imaginary parts.

The long-time behavior of the damped part of $\gamma(t)$ is determined by ν_1, the zero of ϵ_+ having the smallest imaginary part. Numerical values for ν_1 as a function of ν_p^2 can be found from the extensive tables of Fried and Conte.[7] It appears that the most useful variables in this connection are the combinations

$$\alpha=\nu_p^2/2k_BT \tag{90}$$

and

$$\zeta=\nu/(2k_BT)^{1/2}. \tag{91}$$

The numerical results are essentially as follows. When α is smaller than about 3.4 (and either positive or negative), then the imaginary part of ζ is larger than 0.1; under these conditions, which apply for gases at low density, the damping lifetime is of the order of period of oscillation. If, on the other hand, α is very much

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[7] B. D. Fried and S. D. Conte, *The Plasma Dispersion Function* (Academic Press Inc., New York, 1961).

larger than 10, then

$$\zeta\sim\sqrt{\alpha}+O\left(\frac{1}{\sqrt{\alpha}}\right)-i2(\sqrt{\pi})\alpha^2e^{-\alpha}. \tag{92}$$

In this limit, we can replace ν_p by the sound velocity $B(k)$; see Eq. (64). Then, in the limit of large sound velocities, the smallest root is

$$\nu_1\sim B-2i(2\pi k_BT)^{1/2}(B^2/2k_BT)^2e^{-B^2/2k_BT}. \tag{93}$$

The damping rate is very small, and the time dependence of this contribution to $\gamma(t)$ goes as

$$\exp ikBt. \tag{94}$$

This part of the current density propagates as a sound wave.

Furthermore, the relative importance of the persistent and damped contributions to $\gamma(t)$ depends on the sound velocity. When B is large, the persistent free-particle part is small, and the sound-wave part is dominant for a long time (although ultimately it decays to zero). When B is small, the free-particle behavior dominates, and the sound-wave part decays rapidly.

It is interesting to contrast this behavior with what occurs in a plasma. There the parameter ν_p^2 is inversely proportional to k^2. Thus long-wavelength collective variables are associated with very large α, and behave as slightly damped plasma waves. At short wavelengths, on the other hand, α is small, and free-particle behavior is found. [*Note added in proof*. The eigenfunctions are given explicitly by

$$\gamma(v)=[\bar{\varphi}_B(\nu)]^{-1}\,\mathrm{Re}\epsilon_+(\nu)\delta_+(v-\nu)$$

in the notation used above.]

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General Characterization of a Two-Fluid Anisotropic Warm Plasma in Principal Coordinates*

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A macroscopic characterization of a two-fluid compressible plasma in an external constant magnetic field is suggested in this paper by the introduction of two "compressivity tensors," one for the electrons and one for the ions, as new constitutive parameters. A new set of four governing equations is formulated which are mathematically concise and are amenable to meaningful physical interpretation. Because the compressivity tensors and the permittivity tensor are Hermitian and pairwise commutative, a unitary transformation is found which simultaneously diagonalizes the matrix forms of all three parameter tensors. This permits a change of basis for the governing equations to a principal coordinate system. The longitudinal components of the electromagnetic fields can then be decoupled from their transverse components.

I. INTRODUCTION

By far the largest number of published studies on the propagation, scattering, and radiation properties of electromagnetic waves in a plasma environment has been based on the magneto-ionic theory.[1] In this theory the plasma is treated as a homogeneous incompressible medium which is rendered anisotropic under the influence of an external magnetic field; only electron motion is considered. At low frequencies the effects due to the motion of the heavier ions become important, and various authors have extended the magneto-ionic theory to include such effects.[2–6]

When the pressure gradients in a plasma are not negligible, a warm plasma results and the conventional magneto-ionic theory is no longer adequate to describe the properties of wave motion in such a medium. The consideration of plasma compressibility not only increases the mathematical difficulty but also hinders a concise physical interpretation of the equations governing electromagnetic phenomena. Recently the present authors[7,8] introduced a "compressivity tensor" as a new constitutive parameter which can be used to describe medium compressibility in a similar manner as a permittivity tensor is used to describe medium anisotropy. Such a step proved to be advantageous both in the systematic solution of electromagnetic problems in an anisotropic warm plasma and in the physical interpretation of the mathematical formulation.

It is a purpose of this paper to extend the general characterization of an anisotropic warm plasma to a

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