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Kinetic Equation Approach to Phase Transitions

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An exact mathematical discussion of the linearized Enskog–Vlasov equation is given. A criterion for the occurrence of the linear instability is related to a criterion for the occurrence of the bifurcation of the equilibrium stationary solution to the nonlinear Enskog–Vlasov equation. Mathematical results are interpreted physically in connection with phase transitions.

KEY WORDS: Phase transition; kinetic theory; Enskog–Vlasov equation; stability.

1. INTRODUCTION

There is a view of phase transitions, in equilibrium statistical mechanics, which consists in defining a phase transition as a discontinuity in the equilibrium correlation functions when thermodynamic parameters are varied. We shall call this approach to the equilibrium description of phase transitions the equilibrium Kirkwood–Monroe theory[1] of phase transitions, abbreviated as the equilibrium KM theory. Its relation to the other equilibrium theories of phase transition, namely to the Yang–Lee theory, which discusses dependence of the partition function on the thermodynamic parameters, is not yet generally known.[2] The equilibrium KM theory should be more general than the Yang–Lee theory because it should include discussion of the partition function as a function of thermodynamic parameters (as is the Yang–Lee theory) and moreover also as a functional of an external field (equilibrium correlation functions are functional derivatives with respect to an external field). Unfortunately, however, we do not know about any example of such a general study of the partition function.

Discussion of the equilibrium distribution functions usually starts with an equation or set of equations for these functions which is obtained by truncating an

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exact, generally infinite, set of equations for these functions. Truncation brings about, as a rule, a nonlinearity of the starting equation. Phase transition appears as a splitting of solutions to these equation into more branches. Because of a truncation, the equilibrium KM theory is of course not exact from the beginning and it is then difficult to compare it with exact theories, e.g., the Yang–Lee theory. The only solved examples of the equilibrium KM theory so far exist when the basic starting equation is one equation for the one-particle equilibrium distribution function (references are given in Section 3).

A very attractive advantage of the equilibrium KM theory is the possibility of its natural dynamical extension (we shall call it the nonequilibrium Kirkwood–Monroe theory, abbreviated as the nonequilibrium KM theory). The basic equation or set of equations of the equilibrium KM theory is considered as the equation or set of equations for the equilibrium stationary solution to a dynamical equation (equation or a set of equations for the nonequilibrium, time-dependent distribution functions). In other words, by putting

$$f_n(\mathbf{r}_1, \mathbf{v}_1, \mathbf{r}_2, \mathbf{v}_2, \ldots, \mathbf{r}_n, \mathbf{v}_n, t) = f_{n,\mathrm{eq}}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n) \exp[-\tfrac{1}{2}m\beta(v_1^2 + \cdots + v_n^2)] \quad (1)$$

where $\beta = (k_B T)^{-1}$, with k_B the Boltzmann constant, T is temperature, $\mathbf{r}_i$ and $\mathbf{v}_i$ are position and velocity vectors of the ith particle, respectively, t is time, and f_n and $f_{n,\mathrm{eq}}$ are the n-particle distribution function and equilibrium distribution function, respectively, into a dynamical evolution equation or set of equations, one obtains the basic equation of the equilibrium KM theory for the $f_{n,\mathrm{eq}}$. Equilibrium distribution functions are then studied together with the properties of their approach to equilibrium when the thermodynamic parameters are varied. The examples solved so far show that when the thermodynamic parameters have such values that there is a discontinuity in the equilibrium distribution functions (i.e., a phase transition takes place according to the equilibrium KM theory), there is also a discontinuity in the approach to the equilibrium in the sense that in the spectrum of the linearized dynamical operator, points with negative real part occur (the time dependence is assumed $e^{-\lambda t}$), i.e., a linear instability appears. There is, unfortunately, no example of an exact discussion of the nonlinear dynamical equation for distribution functions which could illustrate rigorously the relationship between the equilibrium and nonequilibrium KM theories. Many illustrations could be found, however, in studies of nonequilibrium dissipative structures[3–6]. The basic ideas about the relationship between some mathematical properties of a dynamical equation and physical properties connected with changes of macroscopic structures are the same for both of these theories. The only difference is in the starting dynamical equation (in the flow structures, it is usually the Navier–Stokes equation or its simpler models) and in the Eq. (1). Instead of the right side of (1), a distribution function representing a nonequilibrium stationary solution to the chosen basic dynamical equation is used.

We would like to point out that, however far we are from the exact microscopic dynamics, taking for example the kinetic equation as the basic dynamical equation (in the next sections, it will be the Enskog–Vlasov equation), we are still one stage before postulating a fixed set of macroscopic state variables which is the starting point of most theories which discuss nonequilibrium properties of phase transitions.

The starting equations of these theories could be obtained from basic equations of the nonequilibrium KM theory as equations for coefficients in the decomposition of the distribution functions into a fixed, finite set of functions. Thus, from the mathematical point of view, the choice of a fixed set of macroscopic variables represents a special approximate method of solution to a dynamical equation of the nonequilibrium KM theory. As an illustration, we mention the relation between the starting kinetic equation for the van der Waals gas used by de Sobrino[7] (this kinetic equation is a special case of the Enslog–Vlasov kinetic equation) and the starting set of equation used by Kawasaki[8]. For the values of thermodynamic parameters which are close to its values corresponding to a phase transition, a great change in the properties of the solution is expected. It might be beyond the possibilities of a fixed approximate method to express these changes properly. The choice of the best approximate method for obtaining an asymptotic solution (which is generally different for different values of thermodynamic parameters) or physically the choice of a set of the best macroscopic state variables is one of the results of an exact mathematical discussion of a basic dynamical equation.

In this work, the kinetic equation (i.e., the equation for the one-particle distribution function only) of the Enskog–Vlasov type is taken as the basic dynamical equation. An exact mathematical discussion of some of the properties of its solution and the relationships of mathematical properties to macroscopic physical properties is the main taks of this paper.

The relation of the Enskog–Vlasov equation to exact classical dynamics and reasons for choosing just this equation are discussed only very briefly in Section 2. The equilibrium KM theory corresponding to the Enskog–Vlasov equation (Section 3) includes a generalization of the original Kirkwood–Monroe discussion of hard sphere crystallization[1] and the van Kampen theory of the van der Waals gas.[22] In this section, we also try to give a complete review of works related to the equilibrium KM theory. In Section 4, we discuss exactly the linearized Enskog–Vlasov equation. We prove some general mathematical properties of the linearized Enskog–Vlasov operator (compactness and self-adjointness of some of its parts) and general theorem about the essential parts of the spectrum of this operator. This theorem is a generalization of similar theorems for the linearized Boltzmann and linearized Vlasov operators. Especially interesting, in connection with physical properties of a change of macroscopic structures, is the mathematical problem of finding a criterion for absence of spectral points λ with $\operatorname{Re}\lambda < 0$ (linear instability). According to the theorem about essential spectrum, no point of an essential spectrum could in any case have a real part less than zero. In this way, we have generalized the studies in Refs. 7 and 9–11,[2] which have dealt with the problem of the absence of eigenvalues only (i.e., the problem of linear stability against exponential growth). Equations used in these works are mostly special cases of the linearized Enskog–Vlasov equation. If we apply all approximations used in these works to the criterion for occurrence of bifurcations used in these works to the criterion for occurrence of bifurcation of the equilibrium stationary solution to the nonlinear Enskog–Vlasov equation which is found in

[2] I am grateful to the referee for bringing to my attention Ref. 9.

Section 3, we get criteria identical with those obtained in Refs. 7 and 9–11 for linear stability against exponential growth. At the end of Section 5, we find the simplest model of the linearized Enskog–Vlasov operator for which both criteria coincide exactly. We show further that under some assumptions, the coincidence also takes place for more complicated models. The problem of the residual part of the spectrum in connection with linear stability needs more detailed models (see Section 5) and is left open.

Relations between the equilibrium KM theory and some properties of the dynamical equation form the basis for our physical argument about the correspondence between a linear instability (mathematical property of the linearized Enskog–Vlasov operator) and phase transitions (macroscopic physical property).

Also, other connections between mathematical concepts connected with an evolution equation and macroscopic physical concepts have been proposed. Because they are not mutually independent and because we use some of them in our arguments, we mention the others:

(i) The problem of the macroscopic description of nonequilibrium (but close to equilibrium) states, especially the problem of the selection of the best set of macroscopic state variables (using these variables, the best approximation of the exact asymptotic time development can be achieved) corresponds to the mathematical study of the asymptotic solution to a basic dynamical equation.[12–14]

(ii) The time-displaced correlation function (the cross sections of many scattering experiments, e.g., slow neutron scattering, can be expressed through these functions) are solutions to a basic dynamical equation when appropriate initial conditions are considered.[15,16]

(iii) The nonequilibrium entropy as a physical quantity is closely related to the Liapunov function (the mathematical quantity useful for discussions of nonlinear stability).[5,17]

(iv) The macroscopic universal evolution criterion is related to a variational approach to a basic dynamical equation.[18]

2. KINETIC EQUATION

The equation which will serve us in the next sections as the basic starting equation is the following kinetic equation of the Enskog–Vlasov type:

$$\partial f(\mathbf{r}, \mathbf{v}, t)/\partial t = Rf(\mathbf{r}, \mathbf{v}, t) \tag{2}$$

where

$$R = R_{\mathrm{E}} + R_{\mathrm{V}} - v_\alpha \, \partial/\partial r_\alpha$$

$$R_{\mathrm{E}} f = \int d^2\kappa \, d^3\mathbf{v}_1 \, \sigma^2 (g_\alpha \kappa_\alpha) \, H(g_\alpha \kappa_\alpha) [\eta_{\mathrm{E}}(\mathbf{r} + \tfrac{1}{2}\sigma\kappa) \times f'(\mathbf{r}) f_1'(\mathbf{r} + \sigma\kappa) - \eta_{\mathrm{E}}(\mathbf{r} - \tfrac{1}{2}\sigma\kappa) f(\mathbf{r}) f_1(\mathbf{r} - \sigma\kappa)]$$

$$R_{\mathrm{V}} f = (1/m)[\partial f(\mathbf{r})/\partial v_\alpha] \int d^3\mathbf{r}_1 \, d^3\mathbf{v}_1 \, [\partial V(|\, \mathbf{r} - \mathbf{r}_1 \,|)/\partial r_\alpha] \, \eta_{\mathrm{V}}(\mathbf{r}, \mathbf{r}_1) f_1(\mathbf{r}_1)$$

$f(\mathbf{r}, \mathbf{v}, t)$ is the one-particle distribution function; $\mathbf{r}$, $\mathbf{v}$, and t are position vector velocity vector, and time, respectively; R_E and R_V are the Enskog and Vlasov part of the operator R; m and σ are mass and diameter of the hard-sphere particles under consideration, V is the long-range part of the two-particle potential function; $\mathbf{g} = \mathbf{v}_1 - \mathbf{v}$; $\mathbf{v}' = \mathbf{v} + \varkappa(g_\alpha \kappa_\alpha)$; $\mathbf{v}_1' = \mathbf{v}_1 - \varkappa(g_\alpha \kappa_\alpha)$; $\varkappa$ is a unit vector directed from the center of the sphere with velocity $\mathbf{v}$ to the center with velocity $\mathbf{v}'$; the standard abbreviation $f_1'(\mathbf{r}) \equiv f(\mathbf{r}, \mathbf{v}_1', t)$,... is used; H is a step function, $H(x) = 1$ for $x > 0$ and $H(x) = 0$ for $x < 0$; the function η is supposed to be a functional of $n(\mathbf{r}, t) = \int d^3\mathbf{v} f(\mathbf{r}, \mathbf{v}, t)$,

$$f_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{v}_1, \mathbf{v}_2, t) \equiv \eta(\mathbf{r}_1, \mathbf{r}_2) f(\mathbf{r}_1, \mathbf{v}_1, t) f(\mathbf{r}_2, \mathbf{v}_2, t)$$

where f_2 is two-particle distribution function. We shall write

$$\eta(\mathbf{r}_1, \mathbf{r}_2) \equiv \eta\{n[\tfrac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2), t]; |\mathbf{r}_1 - \mathbf{r}_2|\} \equiv \eta[\tfrac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)]$$

(in the operator R_E, we substitute $\mathbf{r}_1 = \mathbf{r}$, $\mathbf{r}_2 = \mathbf{r} + \sigma\varkappa$). It has been found useful[11,20,21] to express any operator governed by time evolution [in Eq. (2), the operator R] as the sum of reversbile and irreversible parts ($R^{(r)}$ and $R^{(i)}$, respectively) which have different character under the time reversal transformation $\mathbf{r} \to \mathbf{r}$, $\mathbf{v} \to -\mathbf{v}$, $t \to -t$:

$$R^{(r)} f(\mathbf{r}, -\mathbf{v}, -t) = -R^{(r)} f(\mathbf{r}, \mathbf{v}, t), \qquad R^{(i)} f(\mathbf{r}, -\mathbf{v}, -t) = R^{(i)} f(\mathbf{r}, \mathbf{v}, t)$$

It can be found that[20]

$$R_V^{(i)} \equiv 0, \qquad R_V^{(r)} \equiv R_V$$

$$R_E^{(r)} f = \int d^2\varkappa \, d^3\mathbf{v}_1 \, \tfrac{1}{2}\sigma^2 (g_\alpha \kappa_\alpha) \, \eta_E(\mathbf{r} + \tfrac{1}{2}\sigma\varkappa)[f_1'(\mathbf{r} + \sigma\varkappa) f'(\mathbf{r}) + f_1(\mathbf{r} + \sigma\varkappa) f(\mathbf{r})]$$

$$R_E^{(i)} f = R_E f - R_E^{(r)} f$$

If in R_E only terms of order σ^2 are saved, the Boltzmann operator R_B ($R_B^{(r)} \equiv 0$) is obtained.

We have the following reasons for particularly choosing Eq. (2).

(i) The corresponding equation for the equilibrium stationary state is closely related to equations which have been used by Kirkwood and Monroe[1] for hard-sphere crystallization and by van Kampen[22] for the gas–liquid transition of the van der Waals gas. Recently, it has been shown[23,24] that this last equation, for the class of Kac potentials and in the so-called van der Waals limit, is even exact.

(ii) Numerical studies[25,26] of special forms of (2) show that good agreement can be found between calculated and experimental values for some quantities related to time development, especially considering parameters m and σ and functions V, η_E, and η_V as effective quantities (i.e., they have no longer the original physical meaning and they are free to be chosen conveniently).

(iii) Equation (2) includes and generalizes most of the kinetic equations which

have already been used in connection with a discussion of phase transitions.[7,10,27] If we consider Eq. (2) together with the initial condition

$$f(\mathbf{r}, \mathbf{v}, 0) = f_{\text{eq}}(v)(\delta(\mathbf{r} - \mathbf{r}_0) + n + g_{\text{eq}}(\mathbf{r}))$$

where $g = f_2 - f_1 f_1$, then its solution will be the time-displaced correlation function. Closely related is also the classical limit of the equation for the two-particle Green's function, which has been discussed by Mermin.[9]

(iv) Equation (2) is a generalization of the Boltzmann and Vlasov equations and its exact mathematical theory can be considered as organic part of the generalized transport theory.[28]

Although we accept Eq. (2) as the postulated basic equation, we mention some of the problems and difficulties arising when trying to derive such an equation from exact classical dynamics.

(i) In the derivation from the BBGKY hierarchy,[7] it is assumed that the velocity correlations are neglected. Accepting it in some approximate way, we would get an additional term of the Fokker–Planck type.[29]

(ii) Discussion of the Enskog equation from the cluster expansion point of view has been given by Cohen.[30]

(iii) Combining a repulsive and attractive potential, it is difficult to define the stage before and after collision. In Eq. (2), the approximation is used that the long-range attractive part of the potential has no influence on binary collisions. Accepting this in some approximate way (small-angle scatterings), an additive term also of the Fokker–Planck type would appear. We hope to discuss Eq. (2) including a Fokker–Planck term in a subsequent paper.

3. EQUILIBRIUM STATIONARY SOLUTION

We shall look for a stationary solution of the form

$$f(\mathbf{r}, \mathbf{v}) = n(\mathbf{r})\, M(v) \tag{3}$$

where $M(v)$ is the Maxwell distribution

$$M(v) = (m/2\pi)^{3/2}\beta^{3/2} \exp(-\tfrac{1}{2}m\beta v^2)$$

$\beta = (k_B T)^{-1}$, and T is temperature. Further, the dimensionless variables used are $\mathbf{u} = v_0 \mathbf{v}$, $v_2 = (\frac{1}{2}m\beta)^{1/2}$, and the new time t/v_0 will be denoted by t. The Maxwell distribution is now $M(u) = \pi^{-3/2} \exp -u^2$. Inserting (3) into (2) and considering in (2) the Vlasov term only, one gets

$$[\partial n(\mathbf{r})/\partial r_\alpha] + \beta n(\mathbf{r}) \int [\partial V(|\, \mathbf{r} - \mathbf{r}' \,|)/\partial r_\alpha]\, \eta_V(\mathbf{r}, \mathbf{r}')\, n(\mathbf{r}')\, d^3\mathbf{r}' = 0 \tag{4}$$

and considering in (2) the Enskog term only, we get

$$[\partial n(\mathbf{r})/\partial r_\alpha] + \sigma^2 n(\mathbf{r}) \int \eta_E(\mathbf{r} + \tfrac{1}{2}\sigma\boldsymbol{\varkappa})\, n(\mathbf{r} + \sigma\boldsymbol{\varkappa})\, \kappa_\alpha\, d^2\boldsymbol{\varkappa} = 0 \tag{5}$$

If we try to put into (4) the hard core potential function $V \equiv V_{HC}$ and the corresponding $\eta_V \equiv \eta_{HC}$, $V_{HC}(x) = \infty$ for $x < \sigma$ and $V_{HC}(x) = 0$ for $x > \sigma$,

$$\eta_{HC} = H(x - \sigma)\eta_E \tag{6}$$

{i.e., $\exp[-\beta V_{HC}(x)] = H(x - \sigma)$ for all β, thus $\eta_{HC} = \exp[-\beta V_{HC}(x)]\eta_E$ for all β and $-\beta(d/dx)\, V_{HC}(x) \exp[-\beta V_{HC}(x)] = \delta(x - \sigma)$}, we get exactly Eq. (5). This illustrates the evident fact that different dynamical equations can give the identical equation determining the equilibrium stationary state, so that there are many ways of extending the equation for $n(r)$ to the dynamical region. Equation (5) is basically that used by Kirkwood and Monroe[1] for discussion of hard-sphere crystallization. Kobayashi[27] used Vlasov-type collisionless dynamics [in the Eq. (7), only R_V is considered] for dynamical extension of the Kirkwood–Monroe theory. We see that the binary collision Enskog dynamics can be used as well.

The equation for $n(\mathbf{r})$ corresponding to the whole Eq. (2) is

$$\{\partial[\ln n(\mathbf{r})]/\partial r_\alpha\} + \beta \int [\partial V(|\, \mathbf{r} - \mathbf{r}' \,|)/\partial r_\alpha]\, \eta_V(\mathbf{r}, \mathbf{r}')\, n(\mathbf{r}')\, d^3\mathbf{r}'$$

$$+ \sigma^2 \int \eta_E(\mathbf{r} + \tfrac{1}{2}\sigma\boldsymbol{\kappa})\, n(\mathbf{r} + \sigma\boldsymbol{\kappa})\, \kappa_\alpha\, d^2\boldsymbol{\kappa} = 0 \tag{7}$$

According to the equilibrium KM theory,[1,22,31–36] an exact, complete study of (7) yields a good picture of the equilibrium properties of physical system whose dynamics can be represented by Eq. (2). Recently, Strickfaden[33] studied the simplified form of (7) (the so-called van Kampen equation[22]) corresponding physically to the van der Waalls gas which is obtained from (7) supposing that $\eta_V \equiv 1$ and the second term in (7) is approximated by the first term in a Taylor expansion in $\sigma\, |\, \partial n/\partial r\, |$,

$$(\partial/\partial r_\alpha)\left[\phi(n) + \beta \int V(|\, \mathbf{r} - \mathbf{r}' \,|)\, n(\mathbf{r}')\, d^3\mathbf{r}'\right] = 0 \tag{8}$$

(where ϕ is a nonlinear function, different from the logarithm and determined by $\eta_E\{n\}$) or equivalently, the Hammerstein-type equation

$$\phi(n) + \beta \int V(|\, \mathbf{r} - \mathbf{r}' \,|)\, n(\mathbf{r}')\, d^3\mathbf{r}' = \alpha \tag{8'}$$

(α is related to $\| n \|$). This example also shows the incompleteness of the dynamical description given by Eq. (2). Equilibrium statistical mechanics (i.e., the variational principle for the free energy[37]) gives not only Eq. (8), which we obtained here also from (2), but also two other conditions, the first arising from the required property of the second variation, and the second arising when accepting also discontinuous functions in the space of trial function. The second condition is called Maxwell's rule. It has been shown[33] that both of the additional conditions are important for elimination of solutions of (7) corresponding to reality.

It has been proved for many nonlinear operators[38] that in the discussion of the nonlinear eigenvalue problems, a key role is played by the linear eigenvalue problem corresponding to the linearized operator R_l [this is also true, for example, for the Hammerstein equation (8)]. If we suppose (because we cannot prove it) that it is also true for Eq. (7), we can get an explicit condition for bifurcation (physical existence of a change of phase). Inserting $\eta(\mathbf{r}) = n_0[1 + n_1(\mathbf{r})]$ into (7), saving only linear terms in n_1, and performing the Fourier transform

$$n_1(\mathbf{r}) = \int (\exp i\mathbf{k} \cdot \mathbf{r})\, \varphi_1(\mathbf{k})\, d^3\mathbf{k}$$

one the gets condition

$$k + \beta A_{\mathrm{V}}^{(\mathrm{r})}(k) + A_{\mathrm{E},1}^{(\mathrm{r})}(k) + 2A_{\mathrm{E},0}^{(\mathrm{r})}(k) = 0 \tag{9}$$

where the functions A are defined in the next section. Putting $V \equiv V_{HC}$, $\eta_{\mathrm{V}} \equiv \eta_{HC}$, $\sigma = 0$, or $V \equiv 0$, this condition is equivalent to Kirkwood's condition[7] for hard-sphere crystallization, or, in fact, to its slight generalization, because we consider the two-particle distribution function being a functional of the one-particle distribution function. Kirkwood assumed that these two functions are independent. Criterion (9) is also the criterion for the critical temperature of the van der Waals gas when approximations used for obtaining (8) from (7) are applied. A full discussion of the gas–liquid phase transition needs a more detailed discussion of (8) or (8′) because in the transition from gas to liquid there appears a jump in density [norm of $n(\mathbf{r})$]. Such a problem is not already a classical problem of bifurcation.[38]

4. LINEARIZED KINETIC EQUATION

A general rigorous study of the nonlinear Enskog–Vlasov kinetic equation as well as the Boltzmann or Vlasov kinetic equation still seems to be a very difficult mathematical problem. We shall assume that the corresponding linearized equation determines important properties of (2) or that its study is at least a useful first step in the study of (2). There are different possibilities of linearization around different stationary equilibrium solutions. We will discuss here only linearization around $n_0M(u)$, i.e.,

$$f(\mathbf{r}, \mathbf{u}, t) = n_0M(u)[1 + h(\mathbf{r}, \mathbf{u}, t)/M^{1/2}(u)]$$

$$n_0 = \int n(\mathbf{r}, t)\, d^3\mathbf{r}$$

$$h(\mathbf{r}, \mathbf{u}, t) = \int d^3\mathbf{k}(\exp i\mathbf{k} \cdot \mathbf{r})\, \varphi_{\mathbf{k}}(\mathbf{u}, t)$$

Omitting the straightforward calculations, we obtain[20] (see also the appendix)

$$\partial\varphi_{\mathbf{k}}(\mathbf{u}, t)/\partial t = R_l\varphi_{\mathbf{k}}(\mathbf{u}, t) \tag{10}$$

$$R_l = R^{(\mathrm{r})}_{\mathrm{V},l} + R^{(\mathrm{r})}_{\mathrm{E},l} + R^{(\mathrm{i})}_{\mathrm{E},l} - ik_\alpha u_\alpha$$

$$R^{(\mathrm{r})}_{\mathrm{V},l}\varphi_{\mathbf{k}} = -i\beta u_\alpha(k_\alpha/k)\, A^{(\mathrm{r})}_{\mathrm{V}}(k)\, M^{1/2}(u) \int M^{1/2}(u')\, \varphi_{\mathbf{k}}(\mathbf{u}', t)\, d^3\mathbf{u}'$$

$$R^{(\mathrm{r})}_{\mathrm{E},l}\varphi_{\mathbf{k}} = -i[u_\alpha(k_\alpha/k)\, A^{(\mathrm{r})}_{\mathrm{E},1}(k)\, M^{1/2}(u) \int M^{1/2}(u')\, \varphi_{\mathbf{k}}(\mathbf{u}', t)\, d^3\mathbf{u}'$$

$$- (k_\alpha/k)\, A^{(\mathrm{r})}_{\mathrm{E},0}(k)\, M^{1/2}(u) \int M^{1/2}(u')(u_\alpha' - u_\alpha)\, \varphi_{\mathbf{k}}(\mathbf{u}', t)\, d^3\mathbf{u}'] + I^{(\mathrm{r})}_{\mathrm{E}}\varphi_{\mathbf{k}}$$

$$R^{(\mathrm{i})}_{\mathrm{E},l}\varphi_{\mathbf{k}} = -\nu(u)\, \varphi_{\mathbf{k}} - A^{(\mathrm{i})}_{\mathrm{E},0}(k)\, M^{1/2}(u) \int M^{1/2}(u')\, |\, \mathbf{u}' - \mathbf{u}\, |\, \varphi_{\mathbf{k}}(\mathbf{u}', t)\, d^3\mathbf{u}' + I^{(\mathrm{i})}_{\mathrm{E}}\varphi_{\mathbf{k}}$$

$$A^{(\mathrm{r})}_{\mathrm{V}}(k) = (4\pi/k^2)\, n_0[W^{(\mathrm{r})}(V, \eta_{\mathrm{V},0}\,; k, 1) + W^{(\mathrm{r})}(V, \eta_{\mathrm{V},1}\,; k, \tfrac{1}{2})]$$

$$A^{(\mathrm{r})}_{\mathrm{E},0}(k) = \tfrac{1}{2}(4\pi/k^2)\, n_0 W^{(\mathrm{r})}(V_{HC}\,, \eta_{HC,0}\,; k, 1)$$

$$A^{(\mathrm{r})}_{\mathrm{E},1}(k) = (4\pi/k^2)\, n_0 W^{(\mathrm{r})}(V_{HC}\,, \eta_{HC,1}\,; k, \tfrac{1}{2})$$

$$A^{(\mathrm{i})}_{\mathrm{E},0}(k) = (4\pi/k^2)\, n_0 W^{(\mathrm{i})}(V_{HC}\,, \eta_{HC,0}\,; k, 1)$$

$$\nu(u) = n_0\eta_{\mathrm{E},0}\pi^{1/2}\{(\exp -u^2) + [u + (1/2u)]\, \pi^{1/2}\, \mathrm{erf}\,(u)\},\quad \mathrm{erf}\,(x) = 2\pi^{-1/2} \int d\xi\, \exp -\xi^2$$

$$(k_\alpha/k)(4\pi/k^2)\, W^{(\mathrm{r})}(V, a; k, c) = -\int d^3\mathbf{x}\, \sin(c\mathbf{k}\cdot\mathbf{x})[\partial V(x)/\partial x_\alpha]\, a(x)$$

or equivalently

$$W^{(\mathrm{r})}(V, a; k, c) = (1/c^2) \int dx\, [dV(x)/dx]\, a(x)[kcx\cos(kcx) - \sin(kcx)]$$

and

$$(4\pi/k^2)\, W^{(\mathrm{i})}(V, a; k, c) = \int d^3x\, \cos(c\mathbf{k}\cdot\mathbf{x})[\partial V(x)/\partial x_\alpha]\, b_\alpha a(x)\, H(x_\alpha b_\alpha)$$

where b is a fixed, unit vector. According to the definition of η in (2), we have

$$\eta(\mathbf{r}, \mathbf{r}_1) \equiv \eta\{n[\tfrac{1}{2}(\mathbf{r} + \mathbf{r}_1)]; |\, \mathbf{r} - \mathbf{r}_1\, |\}$$
$$= \eta_0 + \eta_1 \frac{n[\frac{1}{2}(\mathbf{r} + \mathbf{r}_1)] - n_0}{n_0} + \cdots$$

where

$$\eta_0 = \eta\{n_0\,; |\, \mathbf{r} - \mathbf{r}_1\, |\};\qquad \eta_1 = n_0(\delta\eta/\delta n)_{n=n_0}$$

The following well-known thermodynamic relations

$$E/n_0 = \tfrac{3}{2}k_{\mathrm{B}}T + (4\pi/2)(n_0/\mathscr{V}) \int_0^\infty dx\, x^2\eta(x)\, V(x)$$

$$p\mathscr{V}/n_0 = k_{\mathrm{B}}T - (4\pi/6)(n_0/\mathscr{V}) \int_0^\infty dx\, x^3\eta(x)\, dV(x)/dx$$

(E is energy, p is pressure) can be used to make clearer a direct physical meaning of the functions A. Expressions which contain V_{HC} and η_{HC} [Eq. (6)] can be simplified, e.g.,

$$W^{(r)}(V_{HC}, \eta_{HC}; k, c) = -(1/c^2)\eta_{E,0}[kc\sigma \cos(kc\sigma) - \sin(kc\sigma)]$$

We prefer, however, the above unified notation. For σk small, we get

$$A^{(i)}_{E,0}(k) = \sigma^2[\pi n_0 \eta_{E,0} + O(\sigma k)^2]$$

$$A^{(r)}_{E,0}(k) = \sigma^2[\sigma k(4\pi/6)\, n_0 \eta_{E,0} + O(\sigma k)^3]$$

$$A^{(r)}_{E,1}(k) = \sigma^2[\sigma k(5/48)\, 4\pi n_0 \eta_{E,1} + O(\sigma k)^3]$$

The explicit form and some properties of the operator I_E are given in the appendix. Equation (10) can be written in a more convenient form,

$$\partial \varphi_{\mathbf{k}}/\partial t = -[ik_\alpha u_\alpha + \nu(u)]\, \varphi_k + K\varphi_{\mathbf{k}} \tag{11}$$

where

$$K = K_1 + K_2$$

$$K_1\varphi_{\mathbf{k}} = -iu_\alpha(k_\alpha/k)[\beta A^{(r)}_V(k) + A^{(r)}_{E,1}(k)]\, M^{1/2}(u) \int M^{1/2}(u')\, \varphi_{\mathbf{k}}(\mathbf{u}', t)\, d^3\mathbf{u}'$$

and K_2 is the rest of the right-hand side of (10). The domain of R_l will be the Hilbert space $L_2(G)$,

$$G \equiv \{u_1 : u_1 \in (-\infty, +\infty)\} \times \{u_2 : u_2 \in (-\infty, +\infty)\} \times \{u_3 : u_3 \in (-\infty, +\infty)\}$$

of complex-valued functions defined over G with inner product

$$(f \cdot g) = \int_G d^3\mathbf{u}\, \bar{f}(\mathbf{u})\, g(\mathbf{u})$$

($\bar{f}$ denotes the complex conjugate of f). The operator K_1 is the linearized Vlasov operator, i.e., nonself-adjoint and compact. In the appendix, it is proved that the operator K_2 is self-adjoint and compact.

The following notation is used: Σ_e denotes the essential spectrum, consisting of a continuous spectrum, eigenvalues of infinite multiplicity, eigenvalues imbedded in the continuous spectrum, and the accumulation points of isolated eigenvalues; Σ_p denotes the isolated eigenvalues which have finite multiplicity; $\varphi_k(\mathbf{u}, t) = e^{-\lambda t}\varphi_{\mathbf{k},\lambda}(\mathbf{u})$. Now, we can prove the following theorem.

Theorem. $\Sigma_e(R_l) = \bar{E}$, where $E \equiv \{\lambda: \lambda = ik_\alpha u_\alpha + \nu(u)\}$ and $\Sigma_p(R_l) = P$, where P is the point set containing those $\lambda \notin E$ such that

$$[\lambda - ik_\alpha u_\alpha - \nu(u)]\, \varphi_{\mathbf{k},\lambda} + K\varphi_{\mathbf{k},\lambda} = 0 \tag{12}$$

possesses a nontrivial solution

$$\varphi_{\mathbf{k},\lambda} \in L_2(G)$$

Proof. In the proof, we use the Weyl–Kato theorem[41]: If T is a closed operator from a Banach space to itself, and A is compact relative to T(i.e., A is T-compact), then T and $T + A$ have the same essential spectrum. From the discussion of the Boltzmann equation,[42] we know that the multiplicative operator in (11) is closed and has the essential spectrum $\Sigma_e = \bar{E}$. According to the Lemma 2 in the appendix, where it is proved that K is compact (evidently also T-compact) and the Weyl–Kato theorem, the essential spectrum of R_l is again $\bar{E}$.

We see that the essential spectra of the linearized Boltzmann $R_{\mathrm{B},l}$ and the linearised Enskog or Enskog–Vlasov operators are identical. For the $R_{\mathrm{B},l}$, it is possible to prove more (i) all spectral points are nonnegative and (ii) the residual spectrum is empty. For the linearized Valsov operator $R_{\mathrm{V},l}$, it can also be proved that the residual spectrum is empty (also Section 5).

The operator K, namely $I_{\mathrm{E}}^{(\mathrm{r})}$ and $I_{\mathrm{E}}^{(\mathrm{i})}$, is very complicated for detailed discussion of (12) (i.e., finding the eigenvalues and corresponding eigenfunctions of R_l and $R_l^{\dagger}$). Because K is compact, we can expect that some simplified models (using degenerate kernels) can be of use. The idea of constructing such models is the same as in study of the Boltzmann equation or transport theory.[39] The experience from these theories teaches, however, that agreement between numerically calculated Σ_p for the exact R_l and modeling $(R_l)_m$ is rather poor. Some models for the Enskog operators have already been proposed,[7,11,40] but they do not possess all the general properties: (i) equation for the equilibrium stationary solution coincides with the linearized equation (7), (ii) $\int d^3\mathbf{u}\, R_l\varphi_{\mathbf{k}}(\mathbf{u}, t) = 0$, (iii) equation has correct behavior under the time reversal transformation, (iv) K_2 is a self-adjoint operator.

5. DYNAMICAL STABILITY

Let us go back to the nonlinear Enskog–Vlasov equation (2). Inserting the separation variable ansatz $f(\mathbf{r}, \mathbf{v}, t) = F(\mathbf{r}, \mathbf{v})\, e^{-\lambda t}$ into (2) (or using Laplace transformation in t), the form of the equation becomes the generalized nonlinear eigenvalue problem for R. The requirement

$$f(\mathbf{r}, \mathbf{u}, t) \xrightarrow{t\to\infty} \pi^{-3/2}(\exp -\beta u^2)\, n(\mathbf{r})$$

(null space of R is prescribed) brings about, moreover, dependence on β. Generally, we have the problem $\mathscr{R}(\beta, \lambda; f) = 0$, where $\mathscr{R}$ is the corresponding nonlinear operator and β and λ the parameters (both λ and β appear nonlineary). The problem $[\mathscr{R}(\beta, \lambda; f) = 0]_{\lambda=0}$ is equivalent to the problem of the equilibrium stationary solution (the equilibrium KM theory), which has been discussed in Section 2.

Because we are interested especially in states which are close to stationary states, the asymptotic property of (2), or equivalently the problem $[\mathscr{R}(\beta, \lambda; f) = 0]_{|\lambda|\in(0,\epsilon)}$ (where ϵ is a small real number) is the most important for us. We know from the equilibrium KM theory that passing β_c, which corresponds to a phase transition,

the solution of $[\mathscr{R}(\beta, \lambda; f) = 0]_{\lambda=0}$ splits into more solutions, i.e., passing β_c, there is a great change in properties of the solution of $[\mathscr{R}(\beta, \lambda; f) = 0]_{\lambda=0}$. It is natural to extend the Kirkwood–Monroe definition of phase transition for nonequilibrium states as a discontinuity of solution to the problem $[\mathscr{R}(\beta, \lambda; f) = 0]_{|\lambda|\in(0,\epsilon)}$. Because of a lack of rigorous discussion of the nonlinear dynamical equation, we cannot prove that from the discontinuity of a solution to the problem $[\mathscr{R}(\beta, \lambda; f) = 0]_{\lambda=0}$ there also follows a discontinuity of solution to the problem $[\mathscr{R}(\beta, \lambda; f) = 0]_{|\lambda|\in(0,\epsilon)}$.

We can support the existence of the above-mentioned property of

$$[\mathscr{R}(\beta, \lambda; f) = 0)]_{|\lambda|\in(0,\epsilon)}$$

if β is close to β_c by the following physical argument. It is mainly macroscopic properties that are changed by phase transitions, thus, discussing nonequilibrium states generally, the macroscopic (also called collective) description or, in other words, the composition of macroscopic (collective) state variables, is changed. It has been proposed[12–14] that there is a close correspondence between the nonequilibrium macroscopic description and properties of an asymptotic solution of (2) or equivalently the problem $[\mathscr{R}(\beta, \lambda; f) = 0]_{|\lambda|\in(0,\epsilon)}$. Thus changes expected physically in nonequilibrium macroscopic properties mean mathematical changes in properties of the solution to $[\mathscr{R}(\beta, \lambda; f) = 0]_{|\lambda|\in(0,\epsilon)}$. In the linearized dynamical equation, it seems natural to expect that discontinuities in the solution to $[\mathscr{R}(\beta, \lambda; f) = 0)]_{|\lambda|\in(0,\epsilon)}$ will occur as a linear instability, i.e., appearance of spectral points with negative real part. Because of a lack of rigorous discussion of $\mathscr{R}(\beta, \lambda; f) = 0$, we cannot go deeper into the relationship between the problem $[\mathscr{R}(\beta, \lambda; f) = 0]_{|\lambda|\in(0,\epsilon)}$ and the problem $[\mathscr{R}_l(\beta, \lambda; f) = 0]_{|\lambda|\in(0,\epsilon)}$, where $\mathscr{R}_l$ is the linearized operator $\mathscr{R}$ around an equilibrium stationary solution. If the points with $\operatorname{Re}\lambda < 0$ are eigenvalues, then the corresponding eigenfunctions play the most important role in the asymptotic behavior. They are generally very different from the eigenfunctions corresponding to the eigenvalues with small but positive real parts which determine an asymptotic solution if there is no spectral point with $\operatorname{Re}\lambda < 0$. Physically, we have just the expected change of macroscopic properties by a phase transition.

According to the theorem about essential spectra (Section 4), no point of the essential spectrum can appear in any case in the left-hand side of the complex λ plane. There is no general statement we can make about eigenvalues and the residual part of the spectrum. Discussion of the residual spectrum, which coincides with discussion of eigenvalues of the adjoint operator $R_l^\dagger$ (for each point λ of the residual spectrum of R_l, the point λ lies in the point spectrum of $R_l^\dagger$), needs very detailed models for R_l (see end of this section) and is not given here. The problem of the absence of eigenvalues with $\operatorname{Re}\lambda < 0$ has been studied for kinetic equations which are special cases of (10) in Ref.[4,7,9,10,19] (If there is no eigenvalue with $\operatorname{Re}\lambda < 0$, the system is linearly stable against exponential growth, but it could be unstable against a different kind of growth.)

Criteria for the absence of eigenvalues with $\operatorname{Re}\lambda < 0$ are also derived later in this section when different models for the operator are used. When comparing these criteria and also criteria obtained in Refs. 7, 9–11, 19 with the criterion (9) for bifurcation of the equilibrium stationary solution to (2) [it is of course necessary to apply

to (9) all approximation used when discussing linear stability], we find that they coincide. This result supports our hypothesis that a discontinuity in the solution to $[\mathscr{R}(\beta, \lambda; f) = 0]_{\lambda=0}$ transfers into a discontinuity in the solution to

$$[\mathscr{R}(\beta, \lambda; f) = 0]_{|\lambda| \in (0,\epsilon)}$$

which appears in the solution to $[\mathscr{R}_l(\beta, \lambda; f) = 0]_{|\lambda| \in (0,\epsilon)}$ as an instability, or, physically that the occurrence of a linear instability in the approach to equilibrium is the non-equilibrium extension of the Kirkwood–Monroe definition of phase transition in equilibrium statistical mechanics.

The physical arguments in Refs. 7 and 9–11 about the relationship between linear instability and phase transitions differ according to different methods used for the transition from the kinetic equation to equilibrium thermodynamics. In Mermin's discussion of the classical limit of the two-particle Green's function, the limit $t \to 0$ gives the two-particle equilibrium distribution function, which is sufficient to determine the thermodynamic potentials (only two-particle interactions are considered). The partition function for the van der Waals gas derived by van Kampen[22] as a functional of the one-particle distribution function has been used by de Sobrino.[7]

We give now a simple derivation of the criterion for the absence of eigenvalues in the left-hand side of the complex λ plane. The simplest model of R_l for which this criterion can be found exactly and coincides exactly with (9) is the following. The operator K_1 is considered exactly, K_2 is approximated by

$$(K_2)_m \varphi_{\mathbf{k}} = -2i(k_\alpha/k) A^{(\mathrm{r})}_{\mathrm{E},0}(k) M^{1/2}(u) u_\alpha \int M^{1/2}(u') \varphi_{\mathbf{k}}(\mathbf{u}', t) d^3\mathbf{u}'$$

and $\nu \equiv 0$. Instead of (10), we then have

$$\partial \varphi_{\mathbf{k}}(\mathbf{u}, t)/\partial t = -ik_\alpha u_\alpha \varphi_{\mathbf{k}}(\mathbf{u}, t) - iu_\alpha M^{1/2}(u)[\beta(k_\alpha/k) A^{(\mathrm{r})}_{\mathrm{V}}(k) + (k_\alpha/k) A^{(\mathrm{r})}_{\mathrm{E},1}(k) + 2(k_\alpha/k) A^{(\mathrm{r})}_{\mathrm{E},0}(k)] \int M^{1/2}(u') \varphi_{\mathbf{k}}(\mathbf{u}', t) d^3\mathbf{u}' \quad (13)$$

This equation gives the exact linearized equation for the equilibrium stationary solution of (2). The operator $(K_2)_m$ does not possesses the general property of self-adjointness derived for the exact K_2 (Lemma 1 in the appendix). The irreversible part of R_l is completely neglected in (13). We introduce $\phi_{\mathbf{k}}(\mathbf{u}, t) = M^{1/2}(u) \varphi_{\mathbf{k}}(u)$, $\phi_{\mathbf{k}}(\mathbf{u}, t) = e^{-i\omega t}\psi_{\mathbf{k}}(\mathbf{u})$ (the direction of $\mathbf{k}$ is chosen to be the direction of the first space coordinate) and we assume normalization $\int \psi_{\mathbf{k}}(\mathbf{u}) d^3\mathbf{u} = 1$ [because Eq. (13) is linear, normalization is arbitrary]. We obtain

$$1 = Z(k, \omega)$$

where

$$Z(k, \omega) = \pi^{-1/2} \int [1/(\omega - ku_1)] u_1(\exp -u_1^2) \times [\beta A^{(\mathrm{r})}_{\mathrm{V}}(k) + A^{(\mathrm{r})}_{\mathrm{E},1}(k) + 2A^{(\mathrm{r})}_{\mathrm{E},0}(k)] du_1 \quad (14)$$

has the form of the Cauchy integral. We shall use the fact that the image of any

point in the upper half plane (of the ω plane) must be either inside the curve $Z(k, \xi + i0)$, $\xi \in (-\infty, +\infty)$, or upon it.[19] We have used the notation $\omega = \xi + i\zeta$. From the Plemelj formulas, one easy gets the real and imaginary parts of the $Z(k, \xi + i0)$, $\xi \in (-\infty, +\infty)$. In order to satisfy (14), one gets two conditions: (1) Im $Z(k, \xi + i0) = 0$, and if this condition is satisfied for a $\xi = \xi_0$, then moving from the left to the right of ξ_0, the sign of Im $Z(k, \xi + i0)$ changes from minus to plus. (2) Re $Z(k, \xi + i0) = 1$. In this way, we get the criterion (9) as the criterion for the absence of eigenvalues with negative real parts.

We shall now show that if (13) is generalized by accepting $\nu = \text{const} \neq 0$ and $(K_2^{(i)})_m = \nu M^{1/2}(u) \int M^{1/2}(u')\, d^3u'$, using the following notation, $k = y\nu$, $\tau\nu = -i\omega$;

$$[k^{-1}A_V^{(r)}(k)]_{k=0} = A_V\,, \qquad [k^{-1}A_{E,1}^{(r)}(k)]_{k=0} = A_{E,1}\,, \qquad [k^{-1}A_{E,0}^{(r)}(k)]_{k=0} = A_{E,0}$$

the criterion for the absence of eigenvalues with negative real parts remains unchanged provided y is small.

Instead of (13), we now have

$$(\tau + iyu_1 + 1)\,\psi_{\mathbf{k}}(\mathbf{u}) = M(u) - iu_\alpha k_\alpha(\beta A_V + A_{E,1} + 2A_{E,0}) \tag{15}$$

The normalization $\int \psi_{\mathbf{k}}(\mathbf{u})\, d^3\mathbf{u} = 1$ has been used. From (15), we obtain

$$1 = I_0 - iy(\beta A_V + A_{E,1} + 2A_{E,0})I_1 \tag{16}$$

where

$$I_n = \int [M(u)\, u_1{}^n/(iyu_1 + \tau + 1)]\, d^3\mathbf{u}$$

For small y, we have

$$I_0 = [1/(1+\tau)] - [y^2/(1+\tau)^3] + O(y^4)$$
$$I_1 = -[iy/(1+\tau)^2] + O(y^3)$$
$$I_2 = [1/(1+\tau)] - [3y^2/(1+\tau)^3] + O(y^4)$$

We shall assume further that $\tau = \tau_0 + \tau_1 y + \tau_2 y^2 + \cdots$. From (16), one obtains

$$\tau_0 = 0, \qquad \tau_1 = 0, \qquad \tau_2 = -(1 + \beta A_V + A_{E,1} + 2A_{E,0}) \tag{17}$$

A criterion for the absence of eigenvalues with negative real parts is $\tau_2 < 0$. We have obtained again the crterion (9).

According to Lemma 1 in the appendix, the operator K_2 is self-adjoint, but the $(K_2)_m$ used above are not self-adjoint operators. For a discussion of the adjoint equation to (10) (i.e., for a discussion of residual spectrum of R_l), it seems to be very important to conserve the self-adjointness in models for K_2. But such models (all properties which models of R_l should possess are summarized at the end of Section 4) are very complicated and the corresponding discussion of eigenvalues is very difficult. If we just try to use

$$(K_2^{(r)})_m{}^\dagger\, \varphi_{\mathbf{k}}{}^\dagger = -2i(k_\alpha/k)\, A_{E,0}^{(r)}(k)\, M^{1/2}(u)\, u_\alpha$$
$$\times \int M^{1/2}(u')\, \varphi_{\mathbf{k}}{}^\dagger(\mathbf{u}', t)\, d^3\mathbf{u}' = (K_2^{(r)})_m\, \varphi_{\mathbf{k}}{}^\dagger$$

in the adjoint equation to (15), we obtain, by the same method as in the discussion of (15),

$$\tau_0^{\dagger} = 0, \quad \tau_1^{\dagger} = 0, \quad \tau_2^{\dagger} = -[1 + \beta A_{\mathrm{V}} + A_{\mathrm{E},1} - 2A_{\mathrm{E},0}(1 + \beta A_{\mathrm{V}} + A_{\mathrm{E},1}] \quad (18)$$

If $A_{\mathrm{E},0} \equiv 0$ (in this case $(K_2)_m = (K_2^{(\mathrm{i})})_m$ is a self-adjoint operator), i.e., if we discuss a model for the Boltzmann–Vlasov kinetic equation, τ_2 and $\tau_2^{\dagger}$ are identical, this means that the residual spectrum is empty. If $A_{\mathrm{E},0} \neq 0$, further calculations using more complicated models are necessary.

6. CONCLUDING REMARKS

The next steps on the way to complete mathematical discussion of the nonlinear Enskog–Vlasov equation (and in this way to a deeper understanding of nonequilibrium properties of some phase transitions) could be: (i) discussion of the residual part of the spectrum and discussion of properties of eigenfunctions corresponding to eigenvalues which are close to zero (physically, the selection of the best macroscopic state variables), (ii) study of different linearized Enskog–Vlasov equations obtained by linearization around different equilibrium stationary solutions to the nonlinear Enskog–Vlasov equation, (iii) using different quasilinear approaches,[45] and (iv) application of the Liapunov theory of stability.

Everything that is known so far about the mathematical properties of the Enskog–Vlasov equation supports the proposed nonequilibrium extension of the equilibrium Kirkwood–Monroe theory of phase transitions.

The next, physically more general, kinetic equation which can be discussed without changing greatly the mathematical methods which were used in this paper is the Enskog–Vlasov kinetic equation with a Fokker–Planck term, or in other words, the Rice–Allnatt kinetic equation with a Vlasov term. A rigorous discussion of more general dynamical equations for one-particle, two-particle, or higher distribution functions still represents a very difficult mathematical problem.

APPENDIX

The linearization of R_{V} is evident and the properties of the $R_{\mathrm{V},l}$ are also well known. We will sketch here the linearization of R_{E} and prove some useful properties of the R_E. The part of $R_{\mathrm{E},l}^{(\mathrm{r})}$ containing $\delta\eta/\delta n$ has the same character as $R_{\mathrm{V},l}$ Its sum we denote as K_1. The rest of $R_{\mathrm{E},l}^{(\mathrm{r})}$ will be denoted as $K_2^{(\mathrm{r})}$,

$$K_2^{(\mathrm{r})}\varphi_{\mathbf{k}}(\mathbf{u}, t) = \tfrac{1}{2} i n_0 \sigma^2 \eta_{\mathrm{E},0} M^{1/2}(u) \int d^2\varkappa \, d^3\mathbf{u}_1 \, (u_{1\alpha} - u_\alpha)$$

$$\times \kappa_\alpha \sin(\sigma k_\alpha \kappa_\alpha) \, M(u_1)[M^{-1/2}(u_1) \, \varphi_{\mathbf{k},1} + M^{-1/2}(u_1') \, \varphi_{\mathbf{k},1}'] \quad (A.1)$$

Linearizing $R_E^{(i)}$, we get

$$\begin{aligned}&\tfrac{1}{2}n_0\sigma^2\eta_{E,0}M^{1/2}(u)\int d^2\varkappa\, d^3\mathbf{u}_1\, M(u_1)(u_{1\alpha}-u_\alpha)\,\kappa_\alpha\\&\quad\times[H(g_\alpha\kappa_\alpha)-H(-g_\alpha\kappa_\alpha)][M^{-1/2}(u_1')\,h_1'(\mathbf{r}+\sigma\varkappa)+M^{-1/2}(u')\,h'(\mathbf{r})\\&\quad-M^{1/2}(u_1)\,h_1(\mathbf{r}-\sigma\varkappa)-M^{-1/2}(u)\,h(\mathbf{r})]\end{aligned}\tag{A.2}$$

The second and the fourth terms are the same as the corresponding terms in the linearized Boltzmann equation. Applying Fourier transform to the third, the second, and the first terms in (A.2), which form the operator $K_2^{(i)}$, one gets

$$\begin{aligned}K_2^{(i)}\varphi_k=&-n_0\sigma^2\eta_{E,0}M^{1/2}(u)\int d^3\mathbf{u}_1\, M^{1/2}(u_1)\int d^2\varkappa\cos(\sigma k_\alpha\kappa_\alpha)\\&\times g_\alpha\kappa_\alpha H(g_\alpha\kappa_\alpha)\,\varphi_{k,1}+n_0\sigma^2\eta_{E,0}M^{1/2}(u)\int d^2\varkappa\, d^3\mathbf{u}_1\, M(u_1)\,g_\alpha\kappa_\alpha\\&\times H(g_\alpha\kappa_\alpha)[M^{-1/2}(u_1')\,\varphi_{k,1}'\cos(\sigma k_\alpha\kappa_\alpha)+M^{-1/2}(u')\,\varphi_k']\end{aligned}$$

The linear integral operator arising from the last term in (A.1) we denote as $I_E^{(r)}$. The linear integral operator arising from the first two terms in (A.2), i.e., the last operator on the right side of (A.3), is denoted as $I_E^{(i)}$.

Lemma 1. All integral operators appearing (as the sum) in the operator $K_2 = K_2^{(r)} + K_E^{(i)}$) are self-adjoint operators.

The proof is evident if we remember that the Jacobian of the transformation $\mathbf{u}, \mathbf{u}_1, \varkappa, \to \mathbf{u}', \mathbf{u}_1', -\varkappa$ is equal to one. The self-adjointness is also evident from the explicit representation of these operators given below.

In order to obtain an explicit form of the integral operators appearing, we use the same manipulation as Grad.[43] We review here only the important steps. (1) In the terms that contain u_1', the transformation $\varkappa \equiv (\vartheta, \epsilon) \to \varkappa_1 \equiv (\tfrac{1}{2}\pi - \vartheta, \epsilon + \pi)$, which changes $\mathbf{u}_1'$ to $\mathbf{u}_1$, is made (ϑ is the angle between $\mathbf{g}$ and $\varkappa$). Equivalently, we can write $\varkappa = (\varkappa_1 \times \mathbf{g} \times \widetilde{\varkappa_1}) \times |\varkappa_1 \times \mathbf{g} \times \varkappa_1|^{-1}$, where $\widetilde{\varkappa_1} = \varkappa_1$ and $\widetilde{(-\varkappa_1)} = \varkappa_1$. (2) In the $I_E^{(i)}$, an arrangement is made such that the step function can be omitted. (3) $\varkappa_1, \mathbf{u}_1 \to \varkappa_1, \mathbf{g}$. (4) $\mathbf{g} = \mathbf{v} + \mathbf{w}$, where $\mathbf{v}$ and $\mathbf{w}$ are vector parallel and perpendicular to $\varkappa_1$, respectively. (5) $\varkappa_1, \mathbf{g} \to \mathbf{v}, \mathbf{w}$. (6) $\mathbf{v} = \mathbf{y}' - \mathbf{y}$.

The result is

$$I_E^{(r)}\varphi_k = \int d^3\mathbf{y}'\, a^{(r)}(\mathbf{y}, \mathbf{y}')\,\varphi_k(\mathbf{y}', t)$$

where

$$\begin{aligned}a^{(r)}(\mathbf{y}, \mathbf{y}') =& in_0\sigma^2\eta_{E,0}\left(\frac{1}{\sqrt{\pi}}\right)^3\frac{1}{|\mathbf{y}'-\mathbf{y}|}\exp\left(-\frac{1}{4}|\mathbf{y}'-\mathbf{y}|^2-\zeta_1^2\right)\\&\times\int d^2\mathbf{w}\sin\left\{\sigma\left[\mathbf{k}\cdot\frac{(\mathbf{y}'-\mathbf{y})\times\mathbf{w}\times\widetilde{(\mathbf{y}'-\mathbf{y})}}{|(\mathbf{y}'-\mathbf{y})\times\mathbf{w}\times(\mathbf{y}'-\mathbf{y})|}\right]\right\}\exp-|\mathbf{w}+\zeta_2|^2\end{aligned}$$

$$I_E^{(i)}\varphi_k = \int d^3\mathbf{y}'\, a^{(i)}(\mathbf{y}, \mathbf{y}')\,\varphi_k(\mathbf{y}', t)$$

where

$$a^{(i)}(\mathbf{y}, \mathbf{y}') = n_0\sigma^2\eta_{E,0}\left(\frac{1}{\sqrt{\pi}}\right)^3 \frac{1}{|\mathbf{y}' - \mathbf{y}|} \exp\left(-\frac{1}{4}|\mathbf{y}' - \mathbf{y}|^2 - \zeta_1^2\right)$$
$$\times \int d^2w \left\{1 + \cos\left[\sigma\left(\mathbf{k} \cdot \frac{(\mathbf{y}' - \mathbf{y}) \times \mathbf{w} \times \widetilde{(\mathbf{y}' - \mathbf{y})}}{|(\mathbf{y}' - \mathbf{y}) \times \mathbf{w} \times (\mathbf{y}' - \mathbf{y})|}\right)\right]\right\}$$
$$\times \exp - |\mathbf{w} + \zeta_2|^2$$

ζ_1 and ζ_2 are vectors parallel and perpendicular, respectively, to the vector $(\mathbf{y}' - \mathbf{y})$,

$$\zeta_1^2 = \frac{1}{4}\frac{(y'^2 - y^2)^2}{|\mathbf{y}' - \mathbf{y}|^2}; \qquad \zeta_2 = \frac{1}{2}\left\{\mathbf{y}'\left[1 - \frac{(y'^2 - y^2)^2}{|\mathbf{y}' - \mathbf{y}|^2}\right] + \mathbf{y}\left[1 + \frac{(y'^2 - y^2)^2}{|\mathbf{y}' - \mathbf{y}|^2}\right]\right\}$$

Lemma 2. The operator $I_E^{(r)}$ and $I_E^{(i)}$ are compact.

For the proof, we use the following theorem[44]: If A is a bounded, normal transformation on the complete Hilbert space and if there exist an integer p such that A^p is compact, then A is itself compact. Using exactly the same method as Grad[43] {because

$$\int d^2\mathbf{w}\,[\exp(-|\mathbf{w} + \zeta_2|^2)]\sin(\cdots) \leqslant \int d^2\mathbf{w} \exp(-|\mathbf{w} + \zeta_2|^2)$$

and similarly in $a^{(i)}(\mathbf{y}, \mathbf{y}')$}, we find that for $p = 3$, the corresponding kernels are square-integrable. This means that the operators $(I_E^{(r)})^3$ and $(I_E^{(i)})^3$ are compact and, according the above theorem, the operators $I_E^{(r)}$ and $I_E^{(i)}$ are also compact. The operator K_1 and all remaining operators in K are evidently compact, so that the whole operator K is compact as well.

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