Kinetics of the relaxation of gas-like systems to equilibrium

Yu. N. Devyatko and V. N. Tronin

Moscow Engineering-Physics Institute

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A density-functional method is used to derive a system of equations for the response function of a slightly nonequilibrium gas-like system in the local approximation. The resulting equations are applicable to the problem of diffusion of interacting Brownian particles in a dense system. Retardation is taken into account in a calculation of the diffusion coefficient in such a system.

The kinetics of relaxation to equilibrium in a system of particles is usually described by means of kinetic equations for one- or two-particle distribution functions.[1–7] When that approach is taken, the kinetic equations are usually derived through an expansion of the Liouville equation in a small parameter (e.g., $\varkappa = nr_0^3 \ll 1$, where n is the density of particles, and r_0 is their interaction range). That approach has some indisputable advantages, but it also has several disadvantages, primarily the complexity of justifying the kinetic equations used for the given physical problem. It becomes particularly difficult to justify the equations for systems of particles in which the gas parameter is not small ($\varkappa \sim 1$).

Another method which could in principle be used to study systems with $\varkappa \sim 1$ is the autocorrelation-function method,[4,9] in which transport coefficients are calculated with the help of the Kubo equations.[4] It was shown in Ref. 9 that this method is completely equivalent to a kinetic-equation method. The method of autocorrelation functions requires an analysis of an entire set of diagrams which arise in the expansion of the exact evolution operator in a small parameter.[4] It is thus difficult to apply this method to specific physical systems. Methods have recently been developed in the quantum theory of many-particle systems for describing relaxation kinetics through the use of a density-functional formalism.[10–13] When that approach is taken in the so-called local approximation,[11] it becomes possible to construct a closed equation for the response function which is valid at all densities.

Our purpose in the present paper is to show that an approach starting from the density-functional method can be extended to classical many-particle systems. This approach proves to be extremely promising for studying collective phenomena and phase transitions in homogeneous and inhomogeneous states in classical kinetics.

1. FREE DIFFUSION AND RESPONSE FUNCTION OF AN EQUILIBRIUM GAS-LIKE SYSTEM

By "gas-like" we mean a system with a binary interaction between particles whose state can be described by specifying a one-particle distribution function $f_1(x)$, where $x = (\mathbf{r},\mathbf{p})$ (r and p are, respectively, the coordinate and momentum of the particle). As systems of this type we might cite a nonideal dense gas, a liquid, and so forth. The description below is carried out for the particular case of a system of particles of a single species. At the end of this section of the paper, we will make the necessary generalizations to the case in which the system contains particles of several species. We consider a system which contains N particles which interact with each other in an arbitrary way. We denote by $H = H(x_1,x_2,...,x_N)$ the Hamiltonian of this system, and we write it as

$$H=\sum_i H_0(\mathbf{p}_i)+\frac{1}{2}\sum_{i\neq j} V(\mathbf{r}_i-\mathbf{r}_j),$$

where $H_0(\mathbf{p})$ is the kinetic energy of one particle, and $V(\mathbf{r})$ is the potential of the binary interaction between particles. A complete description of this system can be found by specifying its N-particle distribution function. According to basic principles of statistical mechanics, the time scale τ_0 of variations in the multiparticle distribution function $f_s(x_1,x_2,...,x_s,t)$ ($s = 2,3,...,N$) is considerably shorter than the time scale of variations in the one-particle function $f_1(x,t)$. At times $t \gg \tau_0$, the multiparticle functions are thus capable of adjusting to accommodate each instantaneous value of $f_1(x,t)$. In other words, at $t \gg \tau_0$ the multiparticle distribution functions are functionals of single-particle distribution functions:[8]

$$f_s(x_1,\ldots,x_s,\ t)\,|_{t\gg\tau_0}=f_s(x_1,\ldots,x_s,\ f_1(x,\ t)),\quad s\geqslant 2. \tag{1.1}$$

The time dependence of f_s is determined exclusively by the dependence $f_1(x,t)$. Knowing the Hamiltonian H, we can calculate the energy of this system[4]

$$E[f_1]=\int H(x_1,\ldots,x_N)f_N(x_1,\ldots,x_N,f_1(x,t))\,dx_1\ldots dx_N, \tag{1.2}$$

and also its entropy,

$$S[f_1]=\int f_N\ln f_N\,dx_1\ldots dx_N. \tag{1.3}$$

It follows from (1.1)–(1.3) that the energy and the entropy are both functionals of the single-particle distribution function $f_1(x,t)$ at $t \gg \tau_0$. In the equilibrium state, the one-particle distribution function is independent of the time, and its value is found from the extremum of the free energy for a given number of particles:

$$F[f_1]=E[f_1]-TS[f_1],\qquad \frac{\delta F}{\delta f_1}=\mu,\qquad \int f(x)\,dx=N. \tag{1.4}$$

Here T is the temperature, and the parameter μ is related to the chemical potential of the system. Using the explicit expression for the Hamiltonian, we can relate the free energy of the system to the two-particle distribution function. We assume that the dependence of the potential energy on the interaction constant λ has been singled out in the Hamiltonian. We then write

$$H\to H_\lambda=\sum_i H_0(\mathbf{p}_i)+\frac{1}{2}\lambda\sum_{i\neq j} V(\mathbf{r}_i-\mathbf{r}_j). \tag{1.5}$$

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In the limit $\lambda\rightarrow 0$, the system reduces to an ideal system; in the limit $\lambda\rightarrow 1$, we obtain a real system. From (1.5) we find that the multiparticle distribution function is a function of the parameter λ: $f_N=f_N(\lambda)$. For the free energy we then find the expression[3]

$$F[f_1]=F_0[f_1]+\frac{1}{2}\int dx_1\,dx_2\int d\lambda\, f_2(x_1,x_2,f,\lambda)\,V(\mathbf{r}_1-\mathbf{r}_2). \tag{1.6}$$

Here F_0 is the free energy of the ideal system, i.e., of the system without an interaction between particles, and $f_2(x_1,x_2,\lambda)$ is the binary distribution function calculated with the help of Hamiltonian (1.5). The quantity F_0 corresponds to a system of particles in which the interaction "has been turned off." On the other hand, this system of particles is not necessarily an ideal gas; it might be a system of particles in an external field or a system of particles which are interacting with a reservoir. For convenience in the discussion below, we introduce a free energy defined for an arbitrary "effective charge":

$$F_g=F_0+\frac{1}{2}\int dx_1\,dx_2\int\limits_0^g d\lambda\, f_2(x_1,x_2,\lambda,f_1)\,V(\mathbf{r}_1-\mathbf{r}_2). \tag{1.7}$$

With $g=1$, the quantity F_g gives us the pure free energy; its derivative with respect to g at $g=1$ determines the increment in the energy of this system because of the binary interaction between particles:

$$\left.\frac{dF_g}{d_g}\right|_{g=1}=E-E_0=\frac{1}{2}\int dx_1\,dx_2\,V(\mathbf{r}_1-\mathbf{r}_2)\,f_2(x_1,x_2,\lambda=1). \tag{1.8}$$

Here

$$E_0=\int H_0(\mathrm{p})\,f_1(x)\,dx$$

is the energy of the system if the binary interaction is ignored.

In accordance with the discussion above, the binary distribution function $f_2(x_1,x_2,\lambda)$ is a functional of the one-particle distribution function $f_1(x)$. The extrema of the functional $F_g[f_1]$ determine the equilibrium distribution function $f_1(x)$ for an arbitrary effective charge:

$$\frac{\delta F_g}{\delta f_1}=\mu,\qquad \int f_1(x)\,dx=N. \tag{1.9}$$

We express the free energy in terms of a static generalized susceptibility (response function), which we define in the following way. We assume that the system considered is in a time-independent external field $eV_{\text{ext}}(x)$. The static response function $\chi(x,x')$ of this system in the external field $eV_{\text{ext}}(x)$ relates the change in the one-particle distribution function, $\delta f_1(x)$, to the external field $eV_{\text{ext}}(x)$ which causes this change:[3,4]

$$\delta f_1(x)=\int \chi(x,x')\,eV_{ext}(x')\,dx'. \tag{1.10}$$

In the limit $e\rightarrow 0$, the response function $\chi(x,x')$ is obviously independent of e. Following Ref. 11, we write definition (1.10) in operator form:

$$\delta f=\chi e V_{ext}. \tag{1.11}$$

For convenience, we will use this form of the definition below where it will not cause any misunderstanding. If the external field does not depend on the momentum $\mathbf{p}$, we find from (1.9) a relationship between fluctuations of the density of this system and the external field which causes this change:

$$\delta n(\mathbf{r})=\int \beta(\mathbf{r},\mathbf{r}')\,eV_{ext}(\mathbf{r}')\,d\mathbf{r}', \tag{1.12}$$

where

$$\beta(\mathbf{r},\mathbf{r}')\equiv\int \chi(\mathbf{r},\mathbf{r}',\mathbf{p},\mathbf{p}')\,d\mathbf{p}\,d\mathbf{p}'.$$

If there is an external field, the free energy of the system in the limit $e\rightarrow 0$ is determined by

$$F_g^{(e)}=F_g+e\int V_{ext}(x)\,f_1(x)\,dx. \tag{1.13}$$

Here F_g is the free energy at $e=0$, found from (1.7). To calculate the linear-response function, we use Eqs. (1.7) with $F=F_g^{(e)}$. We set $e=0$ in (1.7); we then find the following expression for the equilibrium distribution function:

$$f_1=f^{(0)}(x),\qquad \left.\frac{\delta F_g^{e=0}}{\delta f_1}\right|_{f_1=f^{(0)}}=\mu.$$

We write the solution of (1.4) in the limit $e\rightarrow 0$ as the sum $f_1(x)=f^{(0)}(x)+\delta f(x)$. In first order in e we then have

$$\left.\frac{\delta F_g^{(e)}}{\delta f_1}\right|_{f_1=f^{(0)}}+\frac{\delta^2 F_g^{(e)}}{\delta f_1^2}\,\delta f_1+eV_{ext}=\mu,$$

or

$$\delta f_1=-\frac{\delta^2 F_g^{(e)}}{\delta f_1^2}\,eV_{ext}. \tag{1.14}$$

In the limit $e\rightarrow 0$, the quantity $\delta^2F_g^{(e)}/\delta f_1^2$ is independent of e. Comparing (1.11) and (1.14), we find an expression for the generalized susceptibility $\chi_g(x,x')$, calculated for an arbitrary effective charge:

$$\chi_g=-\left[\frac{\delta^2 F_g}{\delta f_1(x)\,\delta f_1(x')}\right]^{-1}. \tag{1.15}$$

Varying (1.7) twice, we find

$$-\chi_g^{-1}=-\chi_0^{-1}+R_g, \tag{1.16}$$

where $\chi_0^{-1}\equiv-\delta^2F_0/\delta f_1^2$ is a generalized susceptibility of the system of noninteracting particles, and

$$R_g(x,x')=\frac{1}{2}\frac{\delta^2}{\delta f_1(x)\,\delta f_1(x')}\times\int\limits_0^g d\lambda\int dx_1\,dx_2\,V(\mathbf{r}_1-\mathbf{r}_2)\,f_2(x_1,x_2,\lambda,f_1). \tag{1.17}$$

The function $R_g(x,x')$ is related to the effective interaction between particles, u, which is in turn given by

$$u=\frac{\delta^2}{\delta f_1^2}(E-E_0)=\frac{1}{2}\frac{\delta^2}{\delta f_1(x)\,\delta f_1(x')}\int dx_1\,dx_2\,V(\mathbf{r}_1-\mathbf{r}_2)\,f_2(x_1,x_2,\lambda=1). \tag{1.18}$$

From (1.17) we find

$$\left.\frac{dR_g}{dg}\right|_{g=1}=u(x,x'). \tag{1.19}$$

Multiplying (1.16) from the left by χ_g and from the right by χ_0, we obtain

$$\chi_g=\chi_0+\chi_0R_g\chi_g, \tag{1.20}$$

or, in expanded form,

$$\chi_g(x,x')=\chi_0(x,x')+\int dx_1\,dx_2\,\chi_0(x.\,x_1)R_g(x_1,x_2)\chi_g(x_2,x'). \tag{1.21}$$

Equation (1.21) can be used to determine the generalized susceptibility of a system of interacting particles if the R_g function is known; relation (1.19) determines the effective interaction in the system.

The free energy F_g can be expressed in terms of the response function $\chi_g(x,x')$. The one-time, single-particle distribution function is related to the binary distribution function in the thermodynamic limit:[3]

$$\langle\delta f(x)\delta f(x')\rangle=f_2(x,x',\lambda)-f_1(x)f_1(x')+\delta(x-x')f_1(x), \tag{1.22}$$

where the average is over the equilibrium state corresponding to Hamiltonian (1.5). According to the fluctuation dissipation theorem,[3] on the other hand, we have

$$\langle\delta f(x)\delta f(x')\rangle=-T\chi(x,x',\lambda). \tag{1.23}$$

From (1.22) and (1.23) we find

$$f_2(x,x',\lambda)=f_1(x)f_1(x')-T\chi(x,x',\lambda)-\delta(x-x')f_1(x). \tag{1.24}$$

Using the expression for the free energy in terms of the binary distribution function, we finally find

$$F_g=F_0+\frac{1}{2}g\int V(\mathbf{r}_1-\mathbf{r}_2)f(x_1)f(x_2)\,dx_1\,dx_2-\frac{1}{2}T\int_0^g d\lambda\int dx_1\,dx_2\,V(\mathbf{r}_1-\mathbf{r}_2)\chi(x_1,x_2,\lambda)-\frac{1}{2}g\int V(\mathbf{r}_1-\mathbf{r}_2)\delta(x_1-x_2)f(x_1)\,dx_1\,dx_2. \tag{1.25}$$

Varying (1.25) twice with respect to the one-particle distribution function, we find the relationship between the R_g function and the generalized susceptibility:

$$R_g(x,x')=gV(\mathbf{r}-\mathbf{r}')-\frac{1}{2}\frac{\delta^2}{\delta f_1(x)\delta f_1(x')}\times T\int_0^g d\lambda\,V(\mathbf{r}_1-\mathbf{r}_2)\chi(x_1,x_2,\lambda)\,dx_1\,dx_2. \tag{1.26}$$

Equations (1.21) and (1.26) constitute a complete system of equations for describing the behavior of an equilibrium gaslike system of arbitrary density. The binary distribution is found from the known response function $\chi(x,x',g)$ [which is a solution of Eqs. (1.21), (1.26)] with the help of relationship (1.24). The effective interaction in the system can be found by differentiating the R_g function with respect to the effective charge g in (1.19). The free energy of this system can also be calculated from (1.25).

Equations (1.21) and (1.26) simplify when we are interested in only the spatial response function $\beta(\mathbf{r},\mathbf{r}')$. For this case, we write $\chi(x,x')$ in the form

$$\chi(x,x',\lambda)=\beta(\mathbf{r},\mathbf{r}',\lambda)\varphi(\mathbf{p})\delta(\mathbf{p}-\mathbf{p}'), \tag{1.27}$$

where $\varphi(\mathbf{p})$ is a normalized Maxwellian distribution. Substituting (1.27) into (1.21) and (1.26), we find

$$\beta(\mathbf{r},\mathbf{r}',g)\equiv\beta_g(\mathbf{r},\mathbf{r}')=\beta^{(0)}(\mathbf{r},\mathbf{r}')+\int d\mathbf{r}_1\,d\mathbf{r}_2\,\beta^{(0)}(\mathbf{r},\mathbf{r}_1)R_g(\mathbf{r}_1,\mathbf{r}_2)\beta_g(\mathbf{r}_2,\mathbf{r}'),$$

$$R_g(\mathbf{r},\mathbf{r}')=gV(\mathbf{r}-\mathbf{r}')-\frac{T}{2}\frac{\delta^2}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}\times\int_0^g\int V(\mathbf{r}_1-\mathbf{r}_2)\beta_\lambda(\mathbf{r}_1,\mathbf{r}_2)\,d\lambda\,d\mathbf{r}_1\,d\mathbf{r}_2. \tag{1.28}$$

2. EQUATIONS FOR THE RESPONSE FUNCTION

Equation (1.28) for the R function is a functional equation. There are no methods for solving such equations. We must accordingly transform (1.28) into a simpler equation (or a system of equations). For this purpose we can take the variational derivative of both sides of (1.28) once, twice, etc. In this fashion we generate a chain of equations which relate functional derivatives. This chain of equations is equivalent to an ordinary Bogolyubov chain. To transform it into a system of ordinary differential equations, we need to carry out a transformation to couple the nth derivative with the $(n-1)$st in the last equation, which contains the variational derivative of highest order n. A transformation of this sort which is "integrally" exact was proposed in Ref. 11. Looking ahead to the derivation of a closed nonfunctional equation for the response function, we use the following approximation of the second functional derivative of the functional $\varphi(\mathbf{x},[\rho])$ (as in Ref. 11):

$$\frac{\delta^2\varphi}{\delta\rho(\mathbf{x}_1)\delta\rho(\mathbf{x}_2)}\approx\delta(\mathbf{x}-\mathbf{x}_1)\delta(\mathbf{x}-\mathbf{x}_2)\frac{d^2\varphi(\mathbf{x},\bar{\rho})}{d\bar{\rho}^2},\qquad \bar{\rho}\equiv\frac{1}{v}\int\rho(\mathbf{x})\,d\mathbf{x},\quad v\equiv\int d\mathbf{x}. \tag{2.1}$$

The meaning and accuracy of this approximation can be clarified by going over to a Fourier representation of $\rho(\mathbf{x})$:

$$\rho(\mathbf{x})=\frac{1}{(2\pi)^3}\int\exp(i\mathbf{k}\mathbf{x})\rho(\mathbf{k})\,d\mathbf{k}. \tag{2.2}$$

We then find

$$\frac{\delta^2\varphi}{\delta\rho(\mathbf{x})\delta\rho(\mathbf{x}')}=\frac{1}{(2\pi)^6}\int\frac{\delta^2\varphi}{\delta\rho(\mathbf{k})\delta\rho(\mathbf{k}')}\times\exp(-i\mathbf{k}\mathbf{x})\exp(-i\mathbf{k}'\mathbf{x}')\,d\mathbf{k}\,d\mathbf{k}'. \tag{2.3}$$

In this case relation (2.1) becomes

$$\frac{\delta^2\varphi}{\delta\rho(\mathbf{k})\delta\rho(\mathbf{k}')}=\exp[i(\mathbf{k}+\mathbf{k}')\mathbf{x}]\frac{d^2}{d\bar{\rho}^2}\varphi(\mathbf{x},\bar{\rho}), \tag{2.4}$$

where $\bar{\rho}\equiv\rho(\mathbf{k}\to0)$.

It follows from (2.4) that approximation (2.1) is exact in the limit $\mathbf{k}, \mathbf{k}' \to 0$. Representation (2.1) is thus "integrally" exact in the sense that the integrals of the two sides of this relation over the variables $\mathbf{x}_1$ and $\mathbf{x}_2$ are equal. The meaning of (2.1) is the same as that of the customary local approximation.[11,12,14] Using local approximation (2.1), we find from (1.28),

$$\beta_g(\mathbf{r}, \mathbf{r}') = \beta^{(0)}(\mathbf{r}, \mathbf{r}') + \int d\mathbf{r}_1\, d\mathbf{r}_2\, \beta^{(0)}(\mathbf{r}, \mathbf{r}_1) R_g(\mathbf{r}_1, \mathbf{r}_2) \beta_g(\mathbf{r}_2, \mathbf{r}'),$$
$$R_g(\mathbf{r}, \mathbf{r}') = gV(\mathbf{r}-\mathbf{r}') - \frac{1}{2} T \frac{d^2}{dn^2} \int_0^g V(\mathbf{r}-\mathbf{r}') \beta_\lambda(\mathbf{r}, \mathbf{r}')\, d\lambda. \tag{2.5}$$

For an unbounded system, it is convenient to write Eqs. (2.5) in the Fourier representation:

$$\beta_g(\mathbf{k}) = \beta^{(0)}(\mathbf{k}) + \beta^{(0)}(\mathbf{k}) R_g(\mathbf{k}) \beta_g(\mathbf{k}),$$
$$R_g(\mathbf{k}) = gV(\mathbf{k}) - \frac{T}{2} \frac{d^2}{dn^2} \int_0^g d\lambda \frac{d\mathbf{p}}{(2\pi)^3} V(\mathbf{p}) \beta_\lambda(\mathbf{p}-\mathbf{k}). \tag{2.6}$$

Equations (2.5) or (2.6) constitute a closed system of integrodifferential equations for the response function $\beta_g(\mathbf{k})$ in the local approximation. For potentials whose Fourier transforms $V(\mathbf{k})$, having an extremum as $|\mathbf{k}| \to 0$, fall off rapidly with increasing $|\mathbf{k}|$, Eqs. (2.6) determine the response function $\beta_g(\mathbf{k} \to 0)$. This function is related to the compressibility

$$\frac{1}{n}\left(\frac{\partial p}{\partial n}\right) = -\beta^{-1}(|\mathbf{k}|=0). \tag{2.7}$$

Relation (2.7) can be used to calculate the equation of state of this system from a given susceptibility $\beta_{g=1}(\mathbf{k}=0)$. It can be shown in a similar way that for this class of systems the local approximation can also be used to calculate the free energy of this system.

For the class of potentials specified above, the local approximation and Eqs. (2.6) (which correspond to the local approximation) are suitable for calculating the response functions of a system over large spatial scales, $k \to 0$.

A qualitatively good agreement with the empirical behavior can also be found for a class of potentials whose Fourier transforms do not have an extremum in the limit $\mathbf{k} \to 0$.

In deriving Eqs. (2.5) and (2.6), we took into account the correlation functions (variational derivatives) of arbitrarily high order. In this sense, Eqs. (2.5) and (2.6) are more "accurate" than, for example, the Kirkwood and Percus-Yevick equations.[4] Such equations should be used only for potentials which have a finite Fourier transform. For other potentials, Eq. (2.5) must be used.

To conclude this section of the paper, we will write out for reference the equations which are found from (1.28) in the approximation which comes after the local approximation. For this purpose we vary Eqs. (1.28) with respect to the density. We determine the functions

$$\beta_g^{(1)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \frac{\delta\beta_g(\mathbf{r}_1, \mathbf{r}_2)}{\delta n(\mathbf{r}_3)}, \qquad R_g^{(1)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \frac{\delta R_g(\mathbf{r}_1, \mathbf{r}_2)}{\delta n(\mathbf{r}_3)}. \tag{2.8}$$

Using the local approximation to calculate $\delta R/\delta_n, \delta_\beta/\delta_n$, we then find from (1.28)

$$R_g(\mathbf{r}, \mathbf{r}') = gV(\mathbf{r}-\mathbf{r}') - \frac{T}{2} \frac{\partial}{\partial n} \int V(\mathbf{r}_1-\mathbf{r}') \beta_g^{(1)}(\mathbf{r}', \mathbf{r}_1, \mathbf{r})\, d\mathbf{r}_1,$$
$$R_g^{(1)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = -\frac{T}{2} \frac{\partial^2}{\partial n^2} \int_0^g \beta_\lambda^{(1)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) V(\mathbf{r}_1-\mathbf{r}_2)\, d\lambda, \tag{2.9}$$
$$\beta_g = \beta_0 + \beta_0 R_g \beta_g, \quad \beta_g^{(1)} = \beta_0^{(1)} R_g \beta_g + \beta_0 R_g^{(1)} \beta_g + \beta_0 R_g \beta_g^{(1)},$$

where

$$\beta_0^{(1)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \equiv \delta\beta_0(\mathbf{r}_1, \mathbf{r}_2)/\delta n(\mathbf{r}_3).$$

Equations (2.9) constitute a closed system of equations for determining the response function β_g in the approximation that follows the local approximation. These equations can be used to calculate response functions which are valid for both large and small length scales, in which cases the equations of the local approximation, (2.5) and (2.6), are not sufficiently accurate.

Equations (2.5) and (2.6) can easily be generalized to multicomponent systems. To make this generalization, we note that for a system of several particle species the free energy can be expressed in terms of the partial binary distribution functions $g_{\alpha\beta}^{(2)}(\mathbf{r}_1, \mathbf{r}_2, \lambda)$ (α and β specify the particle species):

$$F = F_0 + \frac{1}{2} \sum_{\alpha,\beta} \int_0^g \int \int V_{\alpha\beta}(\mathbf{r}, \mathbf{r}') g_{\alpha\beta}^{(2)}(\mathbf{r}, \mathbf{r}', \lambda)\, d\lambda\, d\mathbf{r}'\, d\mathbf{r}. \tag{2.10}$$

Without repeating the arguments which led us to Eqs. (1.21) and (1.26), we immediately write the following results, which are found from (2.10):

$$\beta_{\alpha\beta}(g) = \beta_{\alpha\beta}^{(0)} + \beta_{\alpha\mu}^{(0)} R_{\mu\nu}(g) \beta_{\nu\beta}(g), \tag{2.11}$$
$$R_{\alpha\beta}(g) = gV_{\alpha\beta} - \frac{T}{2} \frac{\delta^2}{\delta n_\alpha\, \delta n_\beta} \int_0^g d\lambda\, V_{\mu\nu} \beta_{\mu\nu}(\lambda).$$

A repeated index in (2.10) and (2.11) implies a summation; $\beta_{\alpha\beta}(g)$ is the partial response function, which is determined from

$$\delta n_\alpha(\mathbf{r}) = \int \beta_{\alpha\beta}(\mathbf{r}, \mathbf{r}') e V_{ext}^{(\beta)}\, d\mathbf{r}'. \tag{2.12}$$

Using the local approximation (2.1) we find from (2.11) a closed system of equations for the partial response functions:

$$\beta_{\alpha\beta}(g) = \beta_{\alpha\beta}^{(0)} + \beta_{\alpha\mu}^{(0)} R_{\mu\nu}(g) \beta_{\nu\beta}(g),$$
$$R_{\alpha\beta}(g) = gV_{\alpha\beta} - \frac{T}{2} \frac{\partial^2}{\partial n_\alpha\, \partial n_\beta} \int_0^g V_{\mu\nu} \beta_{\mu\nu}^{(\lambda)}\, d\lambda. \tag{2.13}$$

Equations (2.13), which are similar to Eqs. (2.5) and (2.6) in terms of their meaning and the nature of the approximations used in their derivation, can be used to calculate the response functions of multicomponent systems. Theories of the liquid state lack a suitable mathematical apparatus for analytic studies of multicomponent systems.[15,16]

3. EQUATIONS FOR THE RESPONSE FUNCTION OF SLIGHTLY NONRELATIVISTIC SYSTEMS

The response-function apparatus developed in the preceding sections of this paper makes it possible to study the kinetics of the relaxation of slightly nonequilibrium systems to equilibrium. According to (1.2) and (1.3), these functions and thus the entropy and energy of this system are functionals of the one-particle distribution functions $f_1(x,t)$ at times greater than the time scales of the variation of the multiparticle distribution functions, τ_0. In real systems, the time τ_0 is the time scale of collisions of particles of this system. Assuming that the system is a relaxing system with a steady-state temperature, we construct the following combination from the energy and the entropy:

$$F(t)=E(t)-TS(t). \tag{3.1}$$

The quantity defined in this manner is the same as the free energy of this system in the equilibrium state. According to (1.2) and (1.3), $F(t)$ is a functional of the distribution function $f_1(x,t)$. By "slightly nonequilibrium" states we mean states for which the functional $F(t)$ has the same form as (1.7):

$$F_g(t)=F_0[f_1]+\frac{1}{2}\int dx_1\,dx_2\int_0^g f_2(x_1,x_2,\lambda,f_1)\,V(\mathbf{r}_1-\mathbf{r}_2)\,d\lambda. \tag{3.2}$$

The time dependence of the functional $F_g(t)$ is governed entirely by the time dependence of the distribution function $f_1(x,t)$. According to definition (3.2), those states (for example) for which the distribution function $f_1(x,t)$ is a functional of its first moments are slightly nonequilibrium states. Definition (3.2) holds for any gas-like system which relaxes over times such that the method of a nonequilibrium statistical operator can be used to describe it at $T=$ const (Ref. 2).

The description of the relaxation to equilibrium based on functional (3.2) thus holds in the final stage of the evolution of the system. We introduce the mean value of the free energy of a nonequilibrium system:

$$\Delta_g[f_1]=\lim_{\tau\to\infty}\frac{1}{\tau}\int_0^\tau F_g(t)\,dt. \tag{3.3}$$

Functional (3.3) reaches an extremum for the equilibrium state $(f_1=f^{(0)})$ of a gas-like system with a number of particles which is not fixed:

$$\left.\frac{\delta\Delta_g}{\delta f}\right|_{f=f^{(0)}}=0. \tag{3.4}$$

If the number of particles is instead fixed, it is convenient to replace (3.3) by the functional

$$\tilde{\Delta}[f_1]=\lim_{\tau\to\infty}\left\{\frac{1}{\tau}\left[\int_0^\tau F_g(t)\,dt-\mu\int_0^\tau f_1(x_1,t)\,dx\,dt\right]\right\}, \tag{3.5}$$

which is at an extremum for an equilibrium system with a fixed number of particles $(\delta\tilde{\Delta}_g/\delta f=0)$.

Functionals (3.3)–(3.5) can be used to determine a generalized susceptibility of a gas-like system. We put the system in a weak external field eV_{ext} which varies over time scales such that the conditions (3.2) for a slight nonequilibrium nature of this system are not violated. We define the response function $\tilde{\chi}$ of this system by

$$\delta f(x,t)=\int\tilde{\chi}(x,x',t,t')\,eV_{\text{ext}}(x',t')\,dx'\,dt'. \tag{3.6}$$

In the case $f_0=f_0(t)$, the response function $\tilde{\chi}$ depends on the time arguments t and t' themselves—not only on their difference. This dependence is conveniently put in the form

$$\tilde{\chi}(x,x',t,t')=\tilde{\chi}(x,x',t-t',t). \tag{3.6a}$$

The dependence of the response function on its second argument is determined exclusively by the time dependence of the one-particle distribution function $f_1(x_1,t)$, of which $\tilde{\chi}$ is a functional. The quantity $\tilde{\chi}$ is related to the static susceptibility χ, introduced earlier, by

$$\chi(x,x')=\int\tilde{\chi}(x,x',\tau,t)\,d\tau. \tag{3.6b}$$

When there is an external field $eV_{\text{ext}}(x,t)$, the functional $F_g^{(0)}$, which is the free energy of the nonequilibrium state in the limit $e\to 0$, is determined by an expression similar to (1.13):

$$F_g^{(e)}=F_g(t)+e\int V_{\text{ext}}(x,t)\,f_1(x,t)\,dx. \tag{3.7}$$

The functional $\Delta_g^{(e)}[f_1]$ is given by

$$\tilde{\Delta}_g^{(e)}[f_1]=\lim_{\tau\to\infty}\left\{\frac{1}{\tau}\left[\int_0^\tau F_g^{(e)}(t)\,dt-\mu\int_0^\tau f_1(x,t)\,dx\,dt\right]\right\}. \tag{3.8}$$

From this point on the arguments are similar to those presented above in the derivation of Eq. (1.20). Varying $\tilde{\Delta}_g[f_1]$ with respect to the distribution function $f_1(x,t)$, and making use of the extremal nature of this functional in the case of the equilibrium value $f_1=f^{(0)}$, we find an equation which determines the response function of the nonequilibrium system:

$$\begin{aligned}\tilde{\chi}_g(x,x',t,t')=\tilde{\chi}_0(x,x',t,t')+\int dx_1\,dx_2\,dt_1\,dt_2&\\ \times\tilde{\chi}_0(x,x_1,t,t_1)\,\tilde{R}_g(x_1,x_2,t_1,t_2)\,\tilde{\chi}_g(x_2,x',t_2,t'),&\end{aligned} \tag{3.9}$$

$$\begin{aligned}\tilde{R}_g(x_1,x_2,t_1,t_2)&=\frac{1}{2}\,\frac{\delta^2}{\delta f(x_1,t_1)\,\delta f(x_2,t_2)}\int_0^\infty d\tau\\ &\times\int_0^g d\lambda\,V(\mathbf{r}_1-\mathbf{r}_2)\,f_\lambda^{(2)}(x_1,x_2,\tau)\,dx_1\,dx_2,\\ \tilde{\chi}_g&=-\left[\frac{\delta^2\Delta_g}{\delta f(x_1,t_1)\,\delta f(x_2,t_2)}\right]^{-1},\end{aligned} \tag{3.10}$$

where $\tilde{\chi}_0$ is the response function of a system of noninteracting particles.

The binary distribution function can be related to the response function by using (as before) the fluctuation dissipation theorem:[3]

$$\begin{aligned}&\langle\delta f(x,t)\,\delta f(x',t)\rangle=-T\int_0^\infty\tilde{\chi}(x,x',\lambda,\tau,t)\,d\tau,\\ &\langle\delta f(x,t)\,\delta f(x',t')\rangle\\ &\quad=f_2(x,x',\lambda,t)-f_1(x,t)\,f_1(x',t)+\delta(x-x')\,f_1(x,t).\end{aligned} \tag{3.11}$$

The binary distribution function f_2 and the response function $\tilde{\chi}$ in (3.11) depend on the time t through the quasiequilibrium one-particle distribution function $f_1(x,t)$, of which they are functionals. Using (3.11) and (3.10), we finally find

$$\tilde{R}_g(x,x',t,t')=gV(\mathbf{r}-\mathbf{r}')\delta(t-t')$$

$$-\frac{T}{2}\frac{\delta^2}{\delta f_1(x,t)\delta f_1(x',t')}$$

$$\times\int_0^g d\lambda\int_0^\infty d\tau\int V(\mathbf{r}_1-\mathbf{r}_2)\tilde{\chi}_g(x_1,x_2,\tau,t')\,dx_1\,dx_2. \qquad (3.12)$$

To transform from the function $\tilde{\chi}$ to the response function $\tilde{\beta}(\mathbf{r},\mathbf{r}',t,t')$ for the density we set

$$\tilde{\chi}_\lambda(x,x',t,t')=\tilde{\beta}_\lambda(\mathbf{r},\mathbf{r}',t,t')\varphi(\mathbf{p},t)\delta(\mathbf{p}-\mathbf{p}'), \qquad (3.13)$$

where $\varphi(\mathbf{p},t)$ is a normalized quasiequilibrium momentum distribution function:

$$\int\varphi(\mathbf{p},t)\,d\mathbf{p}=1. \qquad (3.14)$$

Substituting (3.13) into (3.9) and (3.12), integrating over momentum, and using (1.19), we find

$$\tilde{\beta}_g(z,z')=\tilde{\beta}_0(z,z')+\int dz_1\,dz_2\,\tilde{\beta}_0(z,z_1)\tilde{R}_g(z_1,z_2)\tilde{\beta}_g(z_0,z'),$$

$$\tilde{R}_g(z,z')=gV(\mathbf{r}-\mathbf{r}')\delta(t-t')-\frac{T}{2} \qquad (3.15)$$

$$\times\frac{\delta^2}{\delta n(z)\delta n(z')}\int_0^g d\lambda\int V(\mathbf{r}_1-\mathbf{r}_2)\beta_\lambda(z_1,z_2)\,dz_1\,dz_2, \qquad (3.16)$$

$$z\equiv(\mathbf{r},t).$$

To find a closed equation, we use the local approximation, which in the case at hand is

$$\frac{\delta^2\varphi(z_1,[n])}{\delta n(z)\delta n(z')}\approx\delta(z_1-z)\delta(z_1-z')\frac{d^2}{dn^2}\varphi. \qquad (3.16a)$$

Using (3.16a), we find closed equations for the response function:

$$\beta(z,z')=\beta_0(z,z')+\int dz_1\,dz_2\,\beta_0(z,z_1)\tilde{R}_g(z_1,z_2)\beta_g(z_2,z'),$$

$$\tilde{R}_g(z,z')=gV(\mathbf{r}-\mathbf{r}')\delta(t-t') \qquad (3.17)$$

$$-\frac{T}{2}\frac{d^2}{dn^2}\int_0^g d\lambda V(\mathbf{r}-\mathbf{r}')\beta_\lambda(\mathbf{r},\mathbf{r}',t,t').$$

If the parameters characterizing the ground state of the system are assumed to depend on the time, it is convenient to transform from Eqs. (3.17) to equations for the Fourier components of the response functions:

$$\tilde{\beta}_g(\mathbf{k},\omega)=\tilde{\beta}_0(\mathbf{k},\omega)+\tilde{\beta}_0(\mathbf{k},\omega)\tilde{R}_g(\mathbf{k},\omega)\beta_g(\mathbf{k},\omega),$$

$$\tilde{R}_g(\mathbf{k},\omega)=gV(\mathbf{k})-\frac{T}{2}\frac{d^2}{dn^2}\int_0^g d\lambda\frac{d\mathbf{p}}{(2\pi)^3}V(\mathbf{k}-\mathbf{p})\beta_\lambda(\mathbf{p},\omega).$$

$$(3.18)$$

Equations (3.18) can be used to determine the response function $\tilde{\beta}_g(\mathbf{k}\omega)$ of a slightly nonequilibrium system, which in turn determines the relaxation spectrum of the system under consideration:[17]

$$\beta_{g=1}^{-1}(\mathbf{k},\omega)=0. \qquad (3.19)$$

In the static limit, $\omega\to 0$, Eqs. (3.18) naturally go over into Eqs. (2.6).

Equations (3.18) differ from the equations describing the response function of a Fermi system[11] in that even the local approximation for the $\tilde{R}_g$ function contains a term which depends on the frequency ω. There is thus the hope that the description of the spectrum of this system can be more accurate than that of Ref. 11.

The formal reason for the difference is a difference in the expressions for the fluctuation dissipation theorem in the classical and quantum-mechanical cases. In the classical case, the one-time correlation function $\langle\delta f(x,t)\delta f(x',t)\rangle$ is expressed in terms of the static part of the generalized susceptibility in accordance with (3.11). In the quantum-mechanical case, there is no such correspondence. Equations (3.18) generalize in a natural way to systems consisting of several particle species:

$$\tilde{\beta}_g^{\alpha\beta}(\mathbf{k},\omega)=\tilde{\beta}_0^{\alpha\beta}(\mathbf{k},\omega)+\tilde{\beta}_0^{\alpha\mu}\tilde{R}_g^{\mu\nu}(\mathbf{k},\omega)\tilde{\beta}_g^{\nu\beta}(\mathbf{k},\omega),$$

$$\tilde{R}_g^{\mu\nu}(\mathbf{k},\omega) \qquad (3.20)$$

$$=gV_{\mu\nu}(\mathbf{k})-\frac{T}{2}\frac{\partial^2}{\partial n_\mu\,\partial n_\nu}\int_0^g d\lambda\frac{d\mathbf{p}}{(2\pi)^3}V_{\mu\nu}(\mathbf{p})\beta_\lambda^{\mu\nu}(\mathbf{p}-\mathbf{k},\omega).$$

Here $\tilde{\beta}_g^{\mu\upsilon}(\mathbf{k},\omega)$ are partial response functions of the particles of species α and β, and $V_{\mu\nu}$ is the potential of the binary interaction of a particle of species μ with a particle of species ν.

The relaxation spectra of this multicomponent system can be found from the equation

$$\det[\beta_{\alpha\beta}^{-1}(\mathbf{k},\omega,g=1)]=0, \qquad (3.21)$$

where $\tilde{\beta}_{\alpha\beta}^{-1}(\mathbf{k},\omega,g=1)$ is the matrix which is the inverse of the generalized-susceptibility matrix $\tilde{\beta}_{\alpha\beta}(\mathbf{k},\omega,g=1)$.

4. RELAXATION SPECTRA OF A SYSTEM OF INTERACTING BROWNIAN PARTICLES

Let us use the formalism developed above to study the relaxation spectra of a system of Brownian particles which are interacting with each other, for an arbitrary density of these particles. If the density of the system of Brownian particles is comparable to the density of particles in the medium, there may be a significant change in the properties of the medium: The medium may become polarized. This effect can be taken into account by replacing the "bare" binary interaction potential of the Brownian particles, $V(\mathbf{r})$, by an effective potential $V_{\text{eff}}(\mathbf{r})$ which incorporates the polarization of the medium. The generalized susceptibility $\tilde{\beta}_0(\mathbf{k},\omega)$ of a system of Brownian particles which do not interact with each other can be calculated[3] in the following way:

$$\beta_0(\mathbf{k},\omega)=-\frac{n}{T}\frac{\omega_0(\mathbf{k})}{\omega+\omega_0(\mathbf{k})},\quad \omega_0(\mathbf{k})=-iDk^2, \qquad (4.1)$$

where D is the spatial diffusion coefficient, n is the density of Brownian particles, and T is the temperature of the medium. Using (4.1), we find from (3.18) and (3.19) equations for the relaxation spectrum of this system:

$$1+\frac{n}{T}\frac{\omega_0(\mathbf{k})}{\omega+\omega_0(\mathbf{k})}$$

$$\times\left[V(\mathbf{k})-\frac{T}{2}\frac{d^2}{dn^2}\int_0^1 d\lambda\, V(\mathbf{g})\tilde{\beta}_\lambda(\mathbf{g}-\mathbf{k},\omega)\frac{d\mathbf{g}}{(2\pi)^3}\right]=0. \tag{4.2}$$

Equation (4.2) can be solved in its general form for the quasistatic case $\omega\to 0$. We expand the response function $\tilde{\beta}_\lambda(\mathbf{k}-g,\omega)$ in a series near $\omega=0$ and retain terms up to $\sim\omega$. Substituting this expansion into Eq. (4.2), and solving it, we find the relaxation spectrum of this system:

$$\omega(\mathbf{k})=\tilde{\omega}_0(\mathbf{k})\left[1+\frac{n}{T}V(\mathbf{k})\right.$$

$$\left.-\frac{n}{2}\int_0^1 d\lambda\frac{d\mathbf{g}}{(2\pi)^3}\frac{d^2}{dn^2}\tilde{\beta}_\lambda(\mathbf{k}-\mathbf{g},0)\right], \tag{4.3}$$

$$\tilde{\omega}_0(\mathbf{k})=\omega_0(\mathbf{k})\left[1-\int_0^1 V(\mathbf{g})\frac{\partial^3\tilde{\beta}_\lambda(\mathbf{g}-\mathbf{k},\omega)}{\partial n^2\,\partial\omega}\bigg|_{\omega=0}d\lambda\frac{d\mathbf{g}}{(2\pi)^3}\right]^{-1}.$$

Relations (4.3) can be used to calculate the relaxation spectrum of a system of interacting Brownian particles from a known response function. A further simplification of (4.3) can be achieved in the long-wave limit $k\to 0$, $\omega=0$. From (4.3) we find

$$\omega(\mathbf{k})=-i\tilde{D}k^2,$$

$$\tilde{D}=D\left[1+\frac{nV(0)}{T}-\frac{n}{2}\int_0^1 d\lambda\frac{d\mathbf{g}}{(2\pi)^3}V(\mathbf{g})\frac{d^2}{dn^2}\tilde{\beta}_\lambda(\mathbf{g},0)\right]. \tag{4.4}$$

Relations (4.4) are conveniently rewritten with the help of a binary distribution function $n_2(\mathbf{r},\lambda)$. Making use of the relationship between the response function in the limit $\omega=0$ and binary distribution function (3.11), we find from (4.4)

$$\omega(\mathbf{k})=-i\tilde{D}k^2, \tag{4.5}$$

$$\tilde{D}=D\left[1+\frac{n}{2}\int_0^1 V(\mathbf{r})\frac{d^2}{dn^2}n_2(\mathbf{r},\lambda)\,d\mathbf{r}\,d\lambda\right].$$

Relations (4.5), derived in the local approximation, are nevertheless completely rigorous (for gas-like systems), since the local approximation is exact in the limit $k\to 0$, $\omega\to 0$. Relations (4.5) thus determine the diffusion coefficient of a dense system of interacting Brownian particles. The binary distribution function $n_2(\mathbf{r},\lambda)$ can be calculated with the help of Eqs. (1.24) and (2.6).

The method developed in this paper can be used to calculate the equation of state and the relaxation spectra of classical systems with a binary interaction. In principle, that method can be generalized widely.

Equations (1.20) and (3.9) thus make it possible to carry out a known renormalization procedure[17] which can be outlined as follows: We assume that the response function $\chi_g^{(1)}$ is constructed in terms of the effective interaction $R_g^{(1)}$:

$$\chi_g^{(1)}=\chi_0+\chi_0 R_g^{(1)}\chi_g^{(1)}. \tag{4.6}$$

The total response function χ_g then satisfies the equation

$$\chi_g=\chi_g^{(1)}+\chi_g^{(1)}(R_g-R_g^{(1)})\chi_g. \tag{4.7}$$

This equation can be used to determine (for example) the relaxation spectra of a dense system of particles from the known response function of a system of hard spheres, $\chi_g^{(1)}$. Another possible path for applying this formalism is to use definitions (1.15) and (3.10). The idea is that once we know the response function χ_g we can, according to (2.8), determine the higher-order functions $\beta_g^{(1)},\beta_g^{(2)}$, etc. These results then make it possible to construct the free energy (the functional Δ) of the system as a series in deviations of the density from its mean value:

$$\Delta=\frac{1}{2}\int\beta^{-1}(\mathbf{k},\omega)\,\delta n(\mathbf{k},\omega)\,\delta n^*(\mathbf{k},\omega)\,d\mathbf{k}\,d\omega$$

$$+\frac{1}{3}\int\beta_1^{-1}(\mathbf{k},\omega,\mathbf{k}',\omega')\,\delta n(\mathbf{k},\omega)$$

$$\times\delta n^*(\mathbf{k},\omega)\,\delta n(\mathbf{k},\omega')\,d\mathbf{k}\,d\omega\,d\mathbf{k}'\,d\omega'+\ldots,\qquad \delta n=n-\bar{n}. \tag{4.8}$$

This relation can be used to study phase transitions in the system. According to Ref. 18, the conditions for the occurrence of a phase transition are

$$\frac{\partial\tilde{\beta}_{g=1}^{-1}}{\partial k}\bigg|_{\substack{\omega=\omega_c\\ k=k_c}}=0,\qquad \frac{\partial\tilde{\beta}_{g=1}^{-1}(k,\omega)}{\partial\omega}\bigg|_{\substack{\omega=\omega_c\\ k=k_c}}=0, \tag{4.9}$$

$$\tilde{\beta}_{g=1}^{-1}(k_c,\omega_c)=0.$$

From the expansion of the functional Δ in the ratio $\delta n/\bar{n}$, we easily find an equation for the order parameter—the amplitude of the mode, $\delta n(\mathbf{k},\omega)$—at $k\approx k_c,\omega\approx\omega_c$, through an expansion of the functional Δ in wave vectors at $k\approx k_c$ (Ref. 18). The parameters of the equation for the order parameter are expressed here in terms of a known function, viz., the generalized susceptibility $\beta(\mathbf{k},\omega)$.

Equations (3.18), derived above, are based on the fluctuation-dissipation theorem in its thermodynamic form. In principle, this approach can be generalized to highly nonequilibrium systems through the use of a kinetic version of the fluctuation-dissipation theorem.[3] We will use the general expressions which have been derived to describe the concentration dependence of the diffusion coefficient for atoms (in particular, hydrogen atoms) in metals.

The following features have been identified by now in the concentration dependence of the diffusion of hydrogen in palladium.[19] At low concentrations the diffusion coefficient is essentially independent of the concentration. An increase in the concentration leads to a decrease in the diffusive mobility of hydrogen. In this case, the diffusion coefficient vanishes (a critical slowing) at sufficiently low temperatures. At even lower temperatures, it takes on negative values, which correspond to a stratification of the solid solution into two phases, differing in hydrogen content.[20] As the concentration is increased further, the diffusion coefficient increases to positive values again, goes through a maximum, and then drops sharply.[21] This extremum in the behavior of the diffusion coefficient has yet to be explained, since the existing theories are all restricted in some way. They apply to high temperatures,[22] they apply to low concentrations,[23] or they are based on assumptions whose validity cannot be verified.[19]

The relations derived here can be used to explain the observed behavior without introducing additional assumptions regarding the nature of the diffusion of hydrogen in metals. Hydrogen atoms in a solid, like point detects of any sort, interact with each other in a hard-sphere fashion at $r \leqslant a$, where a is the lattice constant, while they interact as dilatation centers in the case $r \gg a$ (Ref. 24):

$$u(\mathbf{r})=-\varepsilon(a/r)^3 s(\mathbf{n}), \qquad \int s(\mathbf{n})\,d\mathbf{n}=0. \tag{4.10}$$

Let us assume that the nature of the interaction of hydrogen atoms is determined by (4.10) at $r \gtrsim a$ also. Using (3.9), we calculate the response function in this system. For this purpose we go through a renormalization to a short-range interaction ($r \leqslant a$). Using (4.6), we find

$$\beta=\beta^{(1)}+\beta^{(1)}(R-R^{(1)})\beta, \tag{4.11}$$

where β is the response function of a system of hard spheres. We adopt some simplifying assumptions. (a) We assume $R-R^{(1)} \approx u(\mathbf{r})$, where $u(\mathbf{r})$ is determined by (4.10). (b) We write the response function in the system of hard spheres in the approximation of second-order in the density:[4]

$$\beta_1=n\left(\frac{n}{n_0}-1\right)\frac{1}{T}, \qquad n_0\equiv\frac{1}{a^3}. \tag{4.12}$$

Assumption (a) corresponds to the well-known approximation in which a short-range interaction is "dressed" by a long-range interaction treated in the random phase approximation.[4]

The Fourier transform of the potential $u(\mathbf{r})$ depends only weakly on $|\mathbf{k}|$ by virtue of the condition $\int s(\mathbf{n})d\mathbf{n}=0$. Setting $u(\mathbf{k}) \approx u(0) = -\varepsilon a^3$, we then find an expression for the temperature dependence of the diffusion coefficient from (4.5), (4.11), and (4.12):

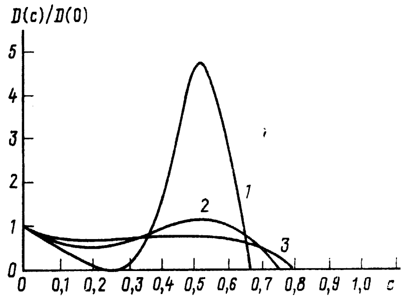

FIG. 1. Relative diffusion coefficient versus the concentration at various temperatures. 1—$\alpha=\varepsilon/T=-3.5$; 2—$\alpha=-2.5$; 3—$\alpha=-2.0$.

$$\frac{D}{D_0}=1+\alpha c-\alpha c\left\{\frac{1+{}^1/{}_2\alpha-\alpha c(1-c)}{2(1+\alpha c(1-c))^2}\right\}, \qquad \alpha\equiv\frac{\varepsilon}{T}. \tag{4.13}$$

Figure 1 shows the behavior $D(c)$ calculated from (4.13) for various temperatures (for various values of α). It follows from this figure that expression (4.13) gives a qualitatively correct description of the experimental situation, including the increase in the diffusion coefficient at $c \approx 0.6$. The $D(c)$ curve runs tangent to the c axis at $c=0.25$; this value agrees with the experimental value of the beginning of the region of critical slowing of diffusion:[19] $c \approx 0.25 \pm 0.05$.

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