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DERIVATION OF GENERALIZED DIFFUSION EQUATIONS

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Generalized form of the diffusion equation is derived from non-Hamiltonian dynamical laws. By application of projection operator method the generalized diffusion equation for the generic configuration distribution function of a system of N_1 immersed particles with arbitrary degrees of internal freedom is obtained. Next it is shown that, if effective quantum mechanical potentials are introduced, a diffusion theory for quantum systems can be formulated with the same conceptual simplicity as has been done in the classical case. Approximations leading towards the ordinary, local and Markovian diffusion equations are discussed.

1. *Introduction*

A considerable attention has been given in recent years to the statistical mechanical study of transport processes of diffusion type. The common Kirkwood–Riseman theory [1–4] of Brownian motion in the configuration space of the systems particles was not able to provide a rigorous justification of the generalized type of diffusion equation. The basic results of this theory are obtained by a somewhat heuristic procedure consisting in the assumption that the frictional, external and intramolecular forces are balanced by a "diffusion" force derivable directly form the position distribution function.

Therefore, many attempts were made to derive the equation of motion for the position distribution function starting directly from fundamental statistical theories. Significant progress was achieved in 1965 when one of the authors [5] (see also [6, 7]) was able to derive the diffusion equation for the configuration distribution function for a classical system of structureless particles immersed in a structureless solvent on the basis of the Lebowitz–Bergmann theory [8] of irreversible Gibbsian ensembles. Starting from an appropriate integro-differential equation, which contains both the terms of the Liouville equation and a stochastic terms describing the interactions with the surroundings a rigorous diffusion theory was developed. Furtheron in that paper a derivation of diffusion equation from the Liouville equation for closed systems was given. Some years later Altenberger [9] derived the generalized form on the Kirkwood–Riseman diffusion equation from the appropriate Liouville equation by applying a similar projection operator method.

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In this paper we address ourselves to the following problems: In Sec. 2, we extend the above mentioned theory (see [5]) to the derivation of the generalized diffusion equation applicable for the determination of the generic configuration distribution function of a subsystem of N_1 immersed particles with arbitrary degrees of internal freedom corresponding to structural constraints. In Sec. 3, we turn towards the task of deriving the generalized diffusion equation describing the dynamical properties of a quantum mechanical system of particles. The derivation is based upon the non-Hamiltonian quantum mechanical theory developed by Ingarden and Kossakowski [10, 11].

In both the classical and the quantum mechanical cases the complete system composed of the subsystem (1) of N_1 immersed particles and the subsystem (2) of N_2 solvent particles ($N_1 \ll N_2$) is supposed to be open, i. e. to interact with its surroundings represented by a thermal reservoir of the temperature T. As a consequence, the dynamics of the entire system is determined by a non-Hamiltonian equation of motion

$$(\partial/\partial t)\,\varrho = \mathscr{L}\varrho, \tag{1.1}$$

where $\mathscr{L}$ is a non-Hamiltonian Liouville superoperator and ϱ stands for the phase-space distribution function or the density operator of the complete system, respectively.

The derivation is based on a projection operator technique [12]. By means of the projection operator G, $G^2 = G$ the quantity ϱ is separated into relevant part ϱ' and irrelevant part ϱ'',

$$\varrho = \varrho' + \varrho'', \quad \varrho' = G\varrho, \quad \varrho'' = (1-G)\varrho. \tag{1.2}$$

Applying the Laplace transforms one can easily obtain the following master equation for the time change of ϱ'

$$(\partial/\partial t)\varrho' = G\mathscr{L}\{\varrho'(t) + A(t)\varrho''(0) + \int_0^t dt_1 A(t-t_1)(1-G)\mathscr{L}\varrho'(t_1)\}, \tag{1.3}$$

where the propagator A is given by

$$A(t) = (1/2\pi i)\int_c dz \exp(zt)\,[z-(1-G)\mathscr{L}]^{-1}. \tag{1.4}$$

Characteristic for the structure of the above master equation is its non-Markovian form, and the fact that the irrelevant part only enters through its initial value.

As we are interested in molecular movements of diffusion type the relevant part ϱ' will be connected with the probability density $\varrho_1(Q^{(1)}, t)$ at time t in the configuration space $Q^{(1)}$ of the N_1 immersed particles. We consider the molecular motions as motions of diffusion type if there exists a closed and causal description of the configuration probability density for all $t > t_0$, when an initial state $\varrho_1(Q^{(1)}, t_0)$ is given. This evidently means a strong restriction to the dynamics of the entire system which nevertheless is fulfilled by a wide class of physical systems.

2. *Derivation of the generalized diffusion equation for a system of classical particles with arbitrary internal degrees of freedom*

Let us consider a system consisting of N_1 immersed particles and N_2 solvent particles, which is in contact with a thermal reservoir of temperature T. Both subsystems are made up of molecules with arbitrary degrees if internal freedom corresponding to structural constraints. Because of the latter the numbers n_i of degrees of freedom are

$$n_i < 3N_i, \quad i = 1, 2, \tag{2.1}$$

where the subscript 1 indicates the subsystem of the immersed particles and 2 stands for the subsystem of the solvent.

Let $Q^{(i)}$ represent the set of generalized coordinates of the ith subsystem and $P^{(i)}$ be the set of the corresponding conjugate momenta. We also use the more concise notation

$$Q = \{Q^{(1)}, Q^{(2)}\} \tag{2.2}$$

for the complete set of configuration coordinates,

$$P = \{P^{(1)}, P^{(2)}\} \tag{2.3}$$

for the complete set of momentum coordinates, and

$$X = \{Q, P\} \tag{2.4}$$

for a point of the phase space of the entire set of molecules. The state of the ensemble is then described by a generic distribution function $\varrho_{N_1+N_2}(X, t)$ in the phase space of the system which is normalized so that

$$\int \varrho_{N_1+N_2}(X, t) dXg = 1, \tag{2.5}$$

with dXg the generic phase space volume element given by

$$dXg = [h^{(n_1+n_2)} N_1! N_2!]^{-1} dX. \tag{2.6}$$

We assume that the temporal evolution of this distribution function is described adequately by an integro-differential equation containing both the terms of the Liouville equation and a stochastic integral term that describes the collisions with its surroundings, i. e. the temperature bath,

$$\begin{aligned}(\partial/\partial t)\varrho_{N_1+N_2}(X, t) = \{H_{N_1+N_2}, \varrho_{N_1+N_2}\} + \int [\varrho_{N_1+N_2}(X')K(X'X) \\ -\varrho_{N_1+N_2}(X)K(XX')] dX'g,\end{aligned} \tag{2.7}$$

where $\{\ldots\}$ is the Poisson bracket,

$$H_{N_1+N_2} = T_{N_1+N_2}(X) + V_{N_1+N_2}(Q) \tag{2.8}$$

is the classical Hamiltonian, the quadratic form

$$T_{N_1+N_2} = T_{N_1} + T_{N_2} = \sum_{i=1}^{2} \tfrac{1}{2} \sum_{l,m=1}^{n_i} C_{lm}^{(i)} p_l^{(i)} p_m^{(i)} = \sum_{i=1}^{2} \tfrac{1}{2} (C^{(i)} P^{(i)}, P^{(i)}), \tag{2.9}$$

with

$$C_{lm}^{(i)} = \sum_{j=1}^{N_i} m_j^{(i)} \frac{\partial \vec{r}_j^{(i)}}{\partial q_l^{(i)}} \cdot \frac{\partial \vec{r}_j^{(i)}}{\partial q_m^{(i)}}, \tag{2.10}$$

the kinetic energy, and $V_{N_1+N_2}$ the potential energy of the system. Now we introduce the following abbreviations

$$(\partial/\partial t)\varrho_{N_1+N_2} = B\varrho_{N_1+N_2} = L\varrho_{N_1+N_2}+S\varrho_{N_1+N_2}, \tag{2.11}$$

where L is the real Liouville operator, which determines the internal motion of the system, and S is the collision operator responsible for the interaction with the thermal reservoir described in terms of impulsive interactions (collisions). The transition kernel $K(X'X)$ represents the probability density per unit time that, the representative point of the system known to be at location X', will be thrown in volume element dX at location X. The stochastic kernel $K(X'X)$ is assumed to be independent on time. As shown by Bergmann and Lebowitz [8] the condition to be obeyed by $K(X'X)$ which is both necessary and sufficient for the approach of the ensemble density to canonicity is

$$\int \{\exp[-\beta H_{N_1+N_2}(X')]K(X'X) - \exp[-\beta H_{N_1+N_2}(X)]K(XX')\}dX' = 0, \tag{2.12}$$

since

$$\{\exp[-\beta H_{N_1+N_2}], H_{N_1+N_2}\} \equiv 0. \tag{2.13}$$

Furthermore, we assume that the effect of the collision operator is to transform only the momenta while the precollision and postcollision configuration coordinates are identical, i. e.

$$K(X'X) = \nu\delta(Q-Q')k(P'P), \tag{2.14}$$

where the quantity ν has the dimension of a frequency and is responsible for the strength of interaction between the system and the temperature bath.

Since we are interested in the distribution function $D_{N_1}(Q^{(1)}, t)$ in the configuration space of the immersed molecules, given by

$$D_{N_1}(Q^{(1)}, t) = \iint dQ^{(2)}dP_g\varrho_{N_1+N_2}(X, t), \tag{2.15}$$

with

$$dP_g = [h^{(n_1+n_2)}N_1!N_2!]^{-1}dP, \tag{2.16}$$

the projection operator G is chosen to be

$$G = \varphi_0 \iint dQ^{(2)}dP_g, \tag{2.17}$$

with

$$\varphi_0 = \varrho_{N_1+N_2}^{\text{eq}}/D_{N_1}^{\text{eq}}, \tag{2.18}$$

where $\varrho^{\text{eq}}_{N_1+N_2}$ and $D^{\text{eq}}_{N_1}$ the corresponding equilibrium distribution functions are denoted. It is easy to verify that G has the desired property to select D_{N_1} (up to a known function), and that it obeys the fundamental requirement of a projection operator $G^2 = G$. (Strictly speaking G is merely an idempotent operator which is not Hermitian in general. However, we maintain the terminology of projection operator technique as it is widly used in recent publications). Under these circumstances one can prove the following identities

$$GS \equiv 0, \tag{2.19}$$

$$S(\varphi_0 D_{N_1}) = 0, \tag{2.20}$$

and

$$GL(\varphi_0 D_{N_1}) = 0. \tag{2.21}$$

We find, furthermore,

$$\iint dQ^{(2)} dPLf(X) = \sum_{k,l=1}^{n_1} \frac{\partial}{\partial q_k} \left[c^{(1)}_{kl} \int dP(-p_l) \int dQ^{(2)} f(X) \right], \tag{2.22}$$

and

$$L(\varphi_0 D_{N_1}) = \sum_{k,l=1}^{n_1} (-p_l) c^{(1)}_{kl} \varphi_0 \left[\frac{\partial}{\partial q_k} - \frac{\partial}{\partial q_k} \ln D^{\text{eq}}_{N_1} \right] D_{N_1}. \tag{2.23}$$

Eqs. (2.19)—(2.23) are obtained under the assumption that the operators G, S and L act in the Hilbert space of all quadratically-integrable functions, i. e. any function $f(X)$ of this space approaches zero sufficiently rapidly for large values of the momentum coordinates and those configuration coordinates which have an infinite range. Taking into account the last five expressions Eqs. (1.3) and (1.4) take the form

$$(\partial/\partial t) D_{N_1}(Q^{(1)}, t) = \sum_{k,m=1}^{n_1} \frac{\partial}{\partial q_k} c_{km} \int dP_g(-p_m) \int dQ^{(2)} \Big\{ A(t) \varrho''_{N_1+N_2}(0)$$
$$+ \frac{1}{v} \int_0^{vt} d\tau A(\tau/v) \sum_{l,n=1}^{n_1} (-p_n) c_{ln} \varphi_0 \left[\frac{\partial}{\partial q_l} - \frac{\partial}{\partial q_l} \ln D^{\text{eq}}_{N_1} \right] D_{N_1} \left(Q^{(1)}, t - \frac{\tau}{v} \right) \Big\} \tag{2.24}$$

and, respectively,

$$A(t) = (1/2\pi i) \int_c dy \exp(vyt) \left[y - L'/v - S' \right]^{-1}, \tag{2.25}$$

where the substitutions $\tau = v(t-t_1)$ and $z = vy$ were introduced and by definition

$$L' = (1-G)L \tag{2.26}$$

and

$$\nu S = S'. \tag{2.27}$$

In most works using projection operator technique the vanishing of the contribution of the initial condition is almost always assumed, not proven rigorously. However, for most non-equilibrium studies one can suppose that as a consequence of its internal dynamics [13] the system has no memory of its initial state. In the particular case when the initial distribution function is given by

$$\varrho_{N_1+N_2}(X; 0) = F(Q^{(1)})\varrho^{\mathrm{eq}}_{N_1+N_2}, \tag{2.28}$$

where $F(Q^{(1)})$ is an arbitrary quadratically integrable function in the configuration space of the 1st system, the source term vanishes.

Eq. (2.24) is the exact form of the general diffusion equation describing the motion of the configuration density $D_{N_1}(Q^{(1)}, t)$ according to the dynamics in consideration. The second term on the right-hand side of the latter equation, termed the memory term, is both non-local in space and non-Markovian with respect to time. At this stage we simplify our original model considering the subsystem of the N_2 solvent particles as identical with the thermal bath, or what is more general, as constituent of the latter. This simplification, which is formally represented by $N_2 = 0$ is, of course, not necessary but it proves very useful for a more detailed discussion. For the solvent is now treated as a continuous heat bath, which interacts with the immersed particles by stochastic collisions of frequency ν, an expansion of $A(t)$ in powers of ν^{-1} is appropiate in the limit of large interactions. If $t \gg \nu^{-1}$ and we furthermore assume that the system has no "memory" for its history, the expansion of the distribution function $D_{N_1}(t-\tau/\nu)$ in powers of (τ/ν) can be carried out. Restricting ourselves to terms of order ν^{-1} in the memory term and assuming that the initial distribution is given by (2.28) we obtain a local and Markovian equation for the time change of D_{N_1}

$$(\partial/\partial t)D_{N_1}(Q^{(1)}, t) = \sum_{k,m=1}^{n_1} \frac{\partial}{\partial q_k} c_{km} \int dP g^{(1)}(-p_m)$$

$$\times \frac{1}{\nu}\int_0^{\nu t} d\tau A_0(\tau) \sum_{l,n=1}^{n_1} (-p_n)c_{ln}\varphi_0 \left[\frac{\partial}{\partial q_l} - \frac{\partial}{\partial q_l}\ln D^{\mathrm{eq}}_{N_1}\right] D_{N_1}(Q^{(1)}, t) \tag{2.29}$$

with

$$A_0(\tau) = (1/2\pi i)\int_c dy \exp(y\tau)\,[y-S']^{-1} \tag{2.30}$$

and

$$\varphi_0 = \varrho^{\mathrm{eq}}_{N_1}/D^{\mathrm{eq}}_{N_1}. \tag{2.31}$$

For a detailed explanation of the transition from the non-local and non-Markovian Eq. (2.24) to the local and Markovian Eq. (2.29) see [5]. At this point we introduce the generic distribution function $\varrho_{N_1}(Q^{(1)}, t)$ given by the renormalization

$$\varrho_{N_1}(Q^{(1)}, t) g_1^{1/2} = D_{N_1}(Q^{(1)}, t) \tag{2.32}$$

with g_1 the determinant

$$g_1 = |\{g_{kl}^{(1)}\}| \tag{2.33}$$

of the metric tensor $\{g_{kl}^{(1)}\}$ of the $Q^{(1)}$—configuration space given by

$$g_{kl}^{(1)} = \sum_{j=1}^{N_1} \frac{\partial \vec{r}_j^{(1)}}{\partial q_k^{(1)}} \cdot \frac{\partial \vec{r}_j^{(1)}}{\partial q_l^{(1)}}, \tag{2.34}$$

where $\vec{r}_j$ represents the three Cartesian coordinates of the j-th mass point. As the volume element $d\tau_1$ of the $Q^{(1)}$—configuration space is given by

$$d\tau_1 = g_1^{1/2} dQ^{(1)}. \tag{2.35}$$

This is the most suitable renormalization of the distribution function in question. Taking into account that the quantity $(\partial/\partial q_l) \ln D_{N_1}^{\text{eq}}$ from Eq. (2.29) can be expressed in the form

$$(\partial/\partial q_l) \ln D_{N_1}^{\text{eq}} = \beta K_l + (\partial/\partial q_l) \ln g_1^{1/2} \tag{2.36}$$

with K_l the mean generalized force given by the following average value

$$K_l = \int dP g^{(1)} \varrho_{N_1}^{\text{eq}} (-\partial V_{N_1}/\partial q_l)/D_{N_1}^{\text{eq}}, \tag{2.37}$$

one obtains the generalized diffusion equation for the generic configuration distribution function of the immersed molecules in the final form

$$(\partial/\partial t) \varrho_{N_1}(Q^{(1)}, t) = \frac{1}{\sqrt{g_1}} \sum_{k,l=1}^{n_1} \frac{\partial}{\partial q_k} \sqrt{g_1}\, D_{kl} \left[\frac{\partial}{\partial q_l} + \beta \frac{\partial U}{\partial q_l} \right] \varrho_{N_1}(Q^{(1)}, t), \tag{2.38}$$

where the generalized diffusion tensor D_{kl} is defined by

$$D_{kl} = \sum_{m,n=1}^{n_1} (1/2\pi i) c_{km} \int dP g^{(1)} \int_c dy\, p_m [S' - y] p_n \varphi_0 c_{ln} [1 - \exp(yvt)]/yv, \tag{2.39}$$

assuming that it approaches a time independent value as t goes to infinity. In the convective part arising from K_l we have introduced the potential of the mean generalized force U in the following convenient way

$$K_l = -(\partial/\partial q_l) U(Q^{(1)}). \tag{2.40}$$

The results obtained in this section are applicable to any type of immersed molecules, flexible or stiff, linear branched or ring shaped, corresponding to the imposed structural constraints. In particular they may be of interest for the investigation of dynamical properties of important polymer (biopolymer) solutions.

3. *Quantum mechanical derivation of generalized diffusion equations*

According to the introduction in this section we consider an open quantum system, composed of N_1 immersed particles (subsystem 1) and N_2 solvent particles (subsystem 2). For simplicity the particles are assumed now to have no degrees of internal freedom. The statistical properties of the complete system are given by the density operator $\varrho_{N_1+N_2}$ which is assumed to be normalized so that $\mathrm{Tr}(\varrho_{N_1+N_2}) = 1$. The time evolution of the density operator is determined by a non-Hamiltonian Liouville operator $\mathscr{L}$, which has a Hamiltonian part

$$(\partial/\partial t)\varrho_{N_1+N_2} = \mathscr{L}\varrho_{N_1+N_2} = (-i/\hbar)\,[H, \varrho_{N_1+N_2}] + \mathscr{D}\varrho_{N_1+N_2}, \tag{3.1}$$

where

$$H = \sum_{1\leqslant i\leqslant N_1+N_2} \frac{p_i^2}{2m_i} + \sum_{1\leqslant i<j\leqslant N_1+N_2} V_{ij}(|\vec{r}_i-\vec{r}_j|) \tag{3.2}$$

is the Hamiltonian determining the internal dynamics of the system, and the dissipator $\mathscr{D}$ arises from the interaction with the systems surroundings, represented by a thermal reservoir of the temperature T (see [10, 11]).

Let us denote the matrix elements of the density operator in the coordinate-spin representation by

$$\langle S_1R_1;\, S_2R_2|\varrho_{N_1+N_2}|S_1'R_1';\, S_2'R_2'\rangle, \tag{3.3}$$

where S_i represents the totality of the spin variables $(\sigma_1, \ldots, \sigma_{N_i})$ of the i-th subsystem, and R_i stands for the complete set of its Cartesian coordinates $(\vec{r}_1, \vec{r}_2, \ldots \vec{r}_{N_i})$, $i = 1, 2$. Now we wish to extract an equation determining the time dependence of the quantity

$$\varrho_1(R_1, t) = \sum_{(S_1)} \langle S_1R_1|\varrho_{N_1}|S_1R_1\rangle, \tag{3.4}$$

where the reduced density operator ϱ_{N_1} is defined by

$$\varrho_{N_1} = \mathop{\mathrm{Tr}}_{(2)}(\varrho_{N_1+N_2}) \tag{3.5}$$

in which $\mathop{\mathrm{Tr}}_{(2)}$ indicates the partial trace over a complete set of variables of the solvent subsystem. At this point, instead of rewriting Eq. (3.1) in terms of the matrix elements (3.3) and defining the dissipator operator $\mathscr{D}$ in the coordinate-spin representation, with the aim of the well-known Wigner transform W [14]

$$W\langle SR|\varrho_{N_1+N_2}|S'R\rangle = (2\pi)^{-3(N_1+N_2)} \int d\Gamma \exp[i(\Gamma, P)]$$

$$\times \left\langle S, R+\frac{\hbar}{2}\Gamma \right| \varrho_{N_1+N_2} \left| S', R-\frac{\hbar}{2}\Gamma \right\rangle, \tag{3.6}$$

where by R we have denoted a complete set (R_1, R_2) of the system position coordinates, and by S the complete set (S_1, S_2) of spin variables, we carry out the transition to the quantum mechanical equation for the quasi-density function $F_{N_1+N_2}(SS'; R; P; t)$ and define $\mathscr{D}$ in terms of the Wigner repesentation. Thus we have

$$
\begin{aligned}
(\partial/\partial t)F_{N_1+N_2}(SS'; R; P; t) = -\sum_{i=1}^{N_1+N_2} \frac{\vec{p}_i}{m_i} \cdot \frac{\partial}{\partial \vec{r}_i} F_{N_1+N_2}(SS'; R; P; t) \\
+(i/(2\pi)^3\hbar) \int d\vec{\tau} \sum_{i\neq j}^{N_1+N_2} \int d\vec{p}_i' \int d\vec{p}_j' \delta(\vec{p}_i'+\vec{p}_j'-\vec{p}_i-\vec{p}_j) \exp\{-i(\vec{\tau}/2) \\
\times [(\vec{p}_i'-\vec{p}_j')-(\vec{p}_i-\vec{p}_j)]\} [V_{ij}(|\vec{r}_i-\vec{r}_j+\tfrac{1}{2}\hbar\vec{\tau}|)-V_{ij}(|\vec{r}_i-\vec{r}_j-\tfrac{1}{2}\hbar\vec{\tau}|)] \\
\times F_{N_1+N_2}(S; S'; R; \vec{p}_1 \ldots \vec{p}_{i-1}\vec{p}_i'\vec{p}_{i+1} \ldots \vec{p}_{j-1}\vec{p}_j'\vec{p}_{j+1} \ldots \vec{p}_{N_1+N_2}; t) \\
+DF_{N_1+N_2}(SS'; R; P; t).
\end{aligned}
\tag{3.7}
$$

As the problem of determining the dissipator operator in the general case is very difficult one, the influence of the systems surroundings is taken into account by defining in the Wigner representation a dissipator of the following simple (linear) form

$$DF_{N_1+N_2}(SS'; R; P; t) = \nu[\varphi_0 \varrho_1(R_1, t) - F_{N_1+N_2}]. \tag{3.8}$$

Here φ_0 represents the quotient $F^{\mathrm{eq}}_{N_1+N_2}/\varrho_1^{\mathrm{eq}}$ with $F^{\mathrm{eq}}_{N_1+N_2}$ the equilibrium quasi-distribution function

$$F^{\mathrm{eq}}_{N_1+N_2}(SS'; R; P) = W\langle SR|\varrho^{\mathrm{eq}}_{N_1+N_2}|S'R\rangle \tag{3.9}$$

and

$$\varrho^{\mathrm{eq}}_{N_1+N_2} = (1/Z_{N_1+N_2}) \exp(-\beta H) \tag{3.10}$$

the equilibrium density operator, where

$$Z_{N_1+N_2} = \mathrm{Tr}\,[\exp(-\beta H)] \tag{3.11}$$

is the (N_1+N_2)-particle partition function. According to the definition (3.4) ϱ_1^{eq} is written as follows

$$\varrho_1^{\mathrm{eq}}(R_1) = \sum_{(S_1)} \langle S_1R_1|\, \underset{(2)}{\mathrm{Tr}}\,(Z^{-1}_{N_1+N_2} \exp(-\beta H))\, |S_1R_1\rangle. \tag{3.12}$$

The parameter ν has the dimension of a frequency and is responsible for the strength of interaction between the system and the temperature bath. As it is necessary for the system's approach to equilibrium, the source term (3.8) vanishes for the canonical quasi-density function $F^{\mathrm{eq}}_{N_1+N_2}$.

As a matter of fact, the Wigner function $F_{N_1+N_2}$ cannot be interpreted as a phase-space density function but, nevertheless, it has a formal similarity to the classical phase-space density and its equation of motion possesses a striking analogy with its classical counterpart. This remarcable parallel will allow us to apply most of the technique which proved successful in the classical theory of generalized diffusion equations. And this is the essential motivation for using $F_{N_1+N_2}$ as an auxiliary function.

The remainder of the derivation is similar to the derivation in the classical case. Employing again Zwanzig's projection operator technique we define the projection operator G by

$$G = \varphi_0 \sum_{(S)} \sum_{(S')} \delta(SS') \int dR_2 \int dP \tag{3.13}$$

with φ_0 defined above. It is then easy to check that G has the desired projection property $G = G^2$ and that for any function $g_{N_1+N_2}$ of the form

$$g_{N_1+N_2}(SS'; R; P; t) = f(R_1, t) F^{\text{eq}}_{N_1+N_2}(SS'; R; P) \tag{3.14}$$

holds

$$G g_{N_1+N_2} = g_{N_1+N_2}. \tag{3.15}$$

Now in analogy with the classical case we abbreviate the first term of the right-hand side of Eq. (3.7) to $L^{(T)}F_{N_1+N_2}(SS'; R; P; t)$ and term $L^{(T)}$ the free particles Liouville operator. Respectively, the second term is abbreviated to $L^{(V)}F_{N_1+N_2}(SS'; R; P; t)$ and $L^{(V)}$ is termed the interaction Liouville operator. Now Eq. (3.7) can be rewritten in the more concise form

$$(\partial/\partial t)F_{N_1+N_2} = (L^{(T)}+L^{(V)})F_{N_1+N_2} + DF_{N_1+N_2} = (L+D)F_{N_1+N_2}, \tag{3.16}$$

with L the quantum mechanical Liouville operator defined as the sum $L = L^{(T)}+L^{(V)}$. The following identities can be proved to hold in the Hilbert space of all quadratically integrable functions

$$GLG \equiv 0, \tag{3.17}$$

$$GD = DG \equiv 0, \tag{3.18}$$

$$\int dR_2 \int dP L f(R; P; t) = \sum_{i=1}^{N_1} \frac{\partial}{\partial \vec{r}_i} \cdot \int dR_2 \int dP(-\vec{p}_i/m_i) f(R; P; t) \tag{3.19}$$

and

$$LGF_{N_1+N_2} = \sum_{j=1}^{N_1} (-\vec{p}_j/m_i)\varphi_0 \left[\frac{\partial}{\partial \vec{r}_j} - \frac{\partial}{\partial \vec{r}_j} \ln \varrho_1^{\text{eq}}(R_1)\right] \varrho_1(R_1, t). \tag{3.20}$$

Substituting the last expressions into Eq. (1.3) we obtain the following equation for the time change of $\varrho_1(R_1, t)$

$$\begin{aligned}(\partial/\partial t)\varrho_1(R_1, t) &= \sum_{i=1}^{N_1} \frac{\partial}{\partial \vec{r}_i} \cdot \int_0^t dt' \sum_{(S)} \sum_{(S')} \delta(SS') \int dR_2 \int dP \\ &\times (-\vec{p}_i/m_i) A(t-t') \sum_{j=1}^{N_1} (-p_j/m_j)\varphi_0 \left[\frac{\partial}{\partial \vec{r}_j} - \frac{\partial}{\partial \vec{r}_j} \ln \varrho_1^{\text{eq}}(R_1)\right] \varrho_1(R_1, t')\end{aligned} \tag{3.21}$$

with the propagator A given by

$$A = (1/2\pi i) \int_c dz \exp(zt)\,[z-(1-G)(L+D)]^{-1}. \tag{3.22}$$

In the above equation the contribution of the initial value $F''_{N_1+N_2}(0)$ vanishes since we have imposed the initial state to be of the form (3.14).

Let us now call our attention to the second term in the brackets on the right-hand side of Eq. (3.21). It is apparent that the convective part of our generalized diffusion equation is due to the inhomogenity of the equilibrium function $\varrho_1^{\mathrm{eq}}(R_1)$ arising from the interparticle interactions. Following a method developed by Morita [15] it is possible to reduce the calculation of the latter quantity to the corresponding classical problem. The crucial point of this theory is the replacement of the Slater sum $S_{N_1+N_2}$, defined by

$$S_{N_1+N_2}(R) = \sum_{(S)} \langle S; R|\exp(-\beta H)|S; R\rangle \prod_{i=1}^{N_1+N_2} \Lambda_i^3, \tag{3.23}$$

with Λ_i the de-Broglie wave length of the i-th particle given by $\Lambda_i = h[2\pi m\,kT]^{-1/2}$, by the Boltzmann factor, according to

$$S_{N_2+N_2}(R) = \exp[-\beta U_{N_1+N_2}(R)]. \tag{3.24}$$

The effective (quantum mechanical) potential $U_{N_1+N_2}$ is expressed in terms of the many particle effective potentials $u_{ijk\ldots}$ by the identity

$$U_{N_1+N_2}(R) = \sum_{i<j} u_{ij} + \sum_{i<j<k} u_{ijk} + \ldots + u_{i_1 i_2 \ldots i_{N1+N2}}, \tag{3.25}$$

where the following connections with the many particle Slater sums $S_2, \ldots, S_{N_1-N_2}$ exist

$$\begin{aligned}
&S_2(\vec{r}_i\vec{r}_j) = \exp[-\beta u_{ij}],\\
&S_3(\vec{r}_i, \vec{r}_j, \vec{r}_k) S_2^{-1}(\vec{r}_i\vec{r}_j) S_2^{-1}(\vec{r}_i\vec{r}_k) S_2^{-1}(\vec{r}_j\vec{r}_k) = \exp[-\beta u_{ijk}],\\
&\vdots\\
&S_{N_1+N_2} \Pi S_{N_1+N_2-1}^{-1} = \exp[-\beta u_{i_1 \ldots i_{N1+N2}}].
\end{aligned} \tag{3.26}$$

However, in many cases of practical interest only the two-particle effective interactions u_{ij} are of relevance

$$u_{ij} = -(1/\beta) \ln S_2(\vec{r}_i\vec{r}_j). \tag{3.27}$$

After Kelbg-Ebeling-Hoffmann [16–19] we get in the case of weak coupling (restriction to linear terms in the two-particle interaction potential V_{ij}, see (3.2)) near the classical limit, i. e. taking into account terms of first and second order in $\hbar^2$ only, the following expression for the many particle Slater sum

$$\begin{aligned}
S_N(R) = \exp\Bigg\{ -\beta \sum_{1\leqslant i<j\leqslant N} V_{ij} - \frac{2\beta}{4!} \sum_{k=1}^{N} (\Lambda_k^2/2\pi)\Delta_k \sum_{1\leqslant i<j\leqslant N} V_{ij}\\
- \frac{3\beta}{6!} \sum_{k=1}^{N} \sum_{l=1}^{N} (\Lambda_k\Lambda_l/2\pi)^2 \Delta_k\Delta_l \sum_{1\leqslant i<j\leqslant N} V_{ij} + O(\hbar^6) \Bigg].
\end{aligned} \tag{3.28}$$

From the combination of Eqs. (3.24)–(3.28) follows that beside the "classical" part V_{ij} the two-particle effective potential contains a quantum mechanical correction of the form

$$u_{ij}^{\mathrm{QM}} = \frac{2}{4!} \sum_{k \in \{i,j\}} (\Lambda_k^2/2\pi)\Delta_k V_{ij} + \frac{3}{6!} \sum_{k,l \in \{i,j\}} \sum (\Lambda_k \Lambda_l/2\pi)^2 \Delta_k \Delta_l V_{ij} + O(\hbar^6), \tag{3.29}$$

whereby

$$u_{ij} = V_{ij} + u_{ij}^{\mathrm{QM}}. \tag{3.30}$$

Now using (3.24) we can identically rewrite the quantity $\varrho_1^{\mathrm{eq}}(R_1)$ in the form

$$\varrho_1^{\mathrm{eq}}(R_1) = \int dR_2 \exp(-\beta U_{N_1+N_2}) [\int dR \exp(-\beta U_{N_1+N_2})]^{-1}, \tag{3.31}$$

which is analogous to the expression for the classical configuration density $D_{N_1}^{\mathrm{eq}}$ of Sec. 2 supposing structureless particles. According to Eqs. (2.37) and (2.40) we can now introduce the mean effective (quantum mechanical) force $\vec{K}_j$ through the average value

$$\vec{K}_j = \int dR_2 \exp[-\beta U_{N_1+N_2}] \left(- \frac{\partial U_{N_1+N_2}}{\partial \vec{r}_j} \right) [\int dR_2 \exp(-\beta U_{N_1+N_2})]^{-1} \tag{3.32}$$

and the effective (quantum mechanical) potential of the mean effective force

$$(\partial/\partial\vec{r}_j) U_{N_1}(R_1) = -\vec{K}_j, \tag{3.33}$$

respectively. Evidently the above definition is identical to

$$\int dR_2 S_{N_1+N_2}(R) = \exp[-\beta U_{N_1}(R_1)]. \tag{3.34}$$

We term the expression

$$S^{(N_1)} = \int dR_2 S_{N_1+N_2}(R) = \sum_{(S_1)} \langle S_1 R_1 | \varrho_{N_1}^{\mathrm{eq}} | S_1 R_1 \rangle \prod_{i=1}^{N_1+N_2} \Lambda_i^3 \tag{3.35}$$

the reduced Slater sum and introduce in the following the many particle effective potentials of the mean force $\phi_{ijk\ldots}$ through

$$U_{N_1} = \sum_{i<j} \phi_{ij} + \sum_{i<j<k} \phi_{ijk} + \ldots + \phi_{i_1 \ldots i_{N_1}}. \tag{3.36}$$

In analogy to (3.26) the effective potentials of the mean force are defined by the reduced many-particle Slater sums $S^{(2)}, S^{(3)}, \ldots, S^{(N_1)}$ according to

$$\begin{aligned} & S^{(2)}(ij) = \exp(-\beta\phi_{ij}), \\ & S^{(3)}(ijk)\,[S^{(2)}(ij) S^{(2)}(ik) S^{(2)}(jk)]^{-1} = \exp(-\beta\phi_{ijk}), \\ & \vdots \\ & S^{(N_1)} \Pi [S^{(N_1-1)}]^{-1} = \exp(-\beta\phi_{i_1 \cdots i_{N_1}}). \end{aligned} \tag{3.37}$$

In order to point out the non-local character of the generalized diffusion equation we now want to make use of the integral representation of the propagator $A(t)$. Let us define the kernel $K(RPt|R'P't')$ corresponding to $A(t-t')$ through

$$A(t-t')f(R, P, t) = \iint dR'dP'K(RPt|R'P't')f(R'P't'), \qquad (3.38)$$

where $f(R, P, t)$ is any quadratically integrale function.

Let us now pass on to the derivation of the normal diffusion equation. For this purpose it is necessary to impose the following very essential conditions. Firstly, we require the de Broglie wave length of the particles to be small compared to the distance characterizing the two-particle interactions (say r_0 is the location of the two-particle potential minimum), i. e.

$$h[2\pi m_i kT]^{-1/2} \ll r_0. \qquad (3.39)$$

It is easy to understand that if (3.39) is not fulfilled the particle movements would be determined by the complete dominance of quantum effects. Furthermore, we suppose that the kernel $K(RPt|R'P't')$ converges rapidly to zero if

$$|r_i - r_i'| \gg l_0, \quad i = 1, 2, \ldots, N_1 + N_2 \qquad (3.40)$$

and

$$t - t' \gg t_0,$$

where l_0 and t_0 are thought to be small quantities, or put into words the "memory" of the kernel K is restricted to time periods of size t_0, while its non-locality spreads over regions of volume l_0^3. We transform now the integrations over t' and R_1' in (3.21) [see also (3.38)] to the new variables

$$\tau = (t-t')/t_0, \qquad \sigma = (R_1 - R_1')/l_0. \qquad (3.41)$$

After expansion of the expression

$$[\partial/\partial\vec{r}_j' + (\partial/\partial\vec{r}_j')U_{N_1}(R_1')]\varrho_1(R_1', t')$$

in powers of t_0 and l_0 and restricting in the integral only to terms of first order we obtain

$$\begin{aligned}(\partial/\partial t)\varrho_1(R_1, t) = {} & \sum_{i=1}^{N_1} \frac{\partial}{\partial\vec{r}_i} \cdot t_0 \int_0^{t/t_0} d\tau \sum_{(S)} \sum_{(S')} \delta(SS') \int dR_2 \int dP \\ & \times(-\vec{p}_i/m_i) \int dP'(l_0)^{3N_1} \int d\sigma \int dR_2' K(RP\tau|R'P'0) \\ & \times \sum_{j=1}^{N_1} (-\vec{p}_j'/m_j)\varphi_0 \left[\frac{\partial}{\partial\vec{r}_j} + \beta\frac{\partial U_{N_1}(R_1)}{\partial\vec{r}_j}\right]\varrho_1(R_1; t). \end{aligned} \qquad (3.42)$$

Now coming back to the old variables (see (3.41)) we introduce the generalized diffusion tensor $D_{ij}(t)$ by

$$D_{ij}(t) = \sum_{(S)} \sum_{(S')} \delta(SS') \int dP \int dR_2 \int dP' \int dR' \int_0^t dt'(-\vec{p}_i/m_i) \times K(RPt'|R'P'0)\,(-p'_j/m_j)\varphi_0(R'P') \tag{3.43}$$

and suppose that for large t it approaches a time independent value D_{ij}. Combination of (3.36) with (3.42) and (3.43) yields finally the normal form of the generalized diffusion equation

$$(\partial/\partial t)\varrho_1(R_1, t) = \sum_{i,j=1}^{N_1} \frac{\partial}{\partial \vec{r}_i} \cdot D_{ij} \Bigg\{ \frac{\partial}{\partial \vec{r}_j} + \beta \sum_{\substack{k=1 \\ (k \neq j)}}^{N_1} (\partial \phi_{jk}/\partial \vec{r}_j) + \beta \sum\sum_{\substack{k<l \\ (k\neq j, l\neq j)}}^{N_1} (\partial \Phi_{jkl}/\partial \vec{r}_j) + \ldots + \beta(\partial \phi_{i_1 \ldots i_{N1}}/\partial \vec{r}_j) \Bigg\}. \tag{3.44}$$

Eq. (3.44) has a striking analogy with the classical generalized diffusion equation (2.38) from Sec. 2. However, in spite of this structural similarity Eq. (3.44) differs essentially from its classical counterpart through the quantum effects manifesting themselves in the generalized diffusion tensor D_{ij} (see (3.43)) and particularly in the effective potentials of the mean generalized force $\phi_{ijk} \ldots$ (see (3.33)) in connection with (3.36). Note that the validity of the quantum mechanical diffusion equation is essentailly connected with assumption (3.39) implying that the system's particles are concerned to be localized over distances of the order r_0.

4. Discussion

In our opinion, the results of the present paper may be of interest for several reasons. First, starting from basic statistical theories the existance of transport equations of diffusion type is justified. Second, the theory presented here gives us the possibility of analysis of the approximations involved (see Sec. 2, 3) and, in this sense, the chance of improvement of the theory. In Sec. 3 it was shown that if effective quantum mechanical interactions are introduced a diffusion theory for quantum systems can be formulated with the same conceptual simplicity as has been attained in the classical case.

Next we want to call attention to the problem of irreversibility involved in our theory. As is well known almost all derivations of transport equations (in general sense) face a difficulty connected with the contradiction between the irreversibility embodied in the final equations and the reversible character of the basic equations of motion. Starting from Hamiltonian dynamics, by means of a procedure of decoupling (as that of neglecting graphs or pertubation terms) irreversibility is just produced by reversibility. This is, of course, mathematically contradictory, since the concept of dynamical semigroups is essentially more general than that of dynamical groups, cf. [10, 11]. The advantage of our theory consists in the fact that at the very beginning we consider dynamical laws of the form proposed by Lebowitz–Bergmann [8] and Ingarden–Kossakowski [10]

$$(\partial/\partial t)\varrho(t) = \mathscr{L}\varrho(t),$$

where $\mathscr{L}$ is a non-Hamiltonian Liouville superoperator on the Hilbert space corresponding to the system. Thus the irreversibility of the final diffusion equations is in complete accordance with the irreversibility of the basic equations of motion. However, in recent time Prigogine and co-workers [20] have presented some new investigations which permit to understand the conceptual problem of irreversibility in a new perspective. They show that kinetic theory, and as a consequence the approach to equilibrium, may be linked to dynamics of a well defined class of initial conditions. Starting from a certain (minimal) level of dynamical complexity the irreversibility of most general physical systems is theoretically justified.

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