ADVANCES IN CHEMICAL PHYSICS

Edited by I. PRIGOGINE
University of Brussels, Brussels, Belgium
and S. A. RICE
University of Chicago, Chicago, U.S.A.

VOLUME XVI

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EDITORIAL BOARD

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INTRODUCTION

In the last decades, chemical physics has attracted an ever-increasing amount of interest. The variety of problems, such as those of chemical kinetics, molecular physics, molecular spectroscopy, transport processes, thermodynamics, the study of the state of matter, and the variety of experimental methods used, makes the great development of this field understandable. But the consequence of this breadth of subject matter has been the scattering of the relevant literature in a great number of publications.

Despite this variety and the implicit difficulty of exactly defining the topic of chemical physics, there are a certain number of basic problems that concern the properties of individual molecules and atoms as well as the behaviour of statistical ensembles of molecules and atoms. This new series is devoted to this group of problems which are characteristic of modern chemical physics.

As a consequence of the enormous growth in the amount of information to be transmitted, the original papers, as published in the leading scientific journals, have of necessity been made as short as is compatible with a minimum of scientific clarity. They have, therefore, become increasingly difficult to follow for anyone who is not an expert in this specific field. In order to alleviate this situation, numerous publications have recently appeared which are devoted to review articles and which contain a more or less critical survey of the literature in a specific field.

An alternative way to improve the situation, however, is to ask an expert to write a comprehensive article in which he explains his view on a subject freely and without limitation of space. The emphasis in this case would be on the personal ideas of the author. This is the approach that has been attempted in this new series. We hope that as a consequence of this approach, the series may become especially stimulating for new research.

Finally, we hope that the style of this series will develop into something more personal and less academic than what has become the standard scientific style. Such a hope, however, is not likely to be completely realized until a certain degree of maturity

has been attained—a process which normally requires a few years.

At present, we intend to publish one volume a year, but this schedule may be revised in the future.

In order to proceed to a more effective coverage of the different aspects of chemical physics, it has seemed appropriate to form an editorial board. I want to express to them my thanks for their cooperation.

I. PRIGOGINE

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CONTENTS

THEORY OF QUANTUM BROWNIAN MOTION

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CONTENTS

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1. INTRODUCTION

For several years, much interest has been raised by the "microscopic" justification of the Brownian motion theory. This theory was developed initially by Einstein and Smoluchowsky in terms of semi-phenomenological arguments and later elaborated by Langevin and others.[1] These authors describe the effects of the fluid particles (of mass m) on Brownian particles (of mass $M \gg m$) in a stochastic fashion. Their results are summarized in the well-known Fokker–Planck equation satisfied by the distribution function of the heavy particle in its position and momentum space. All descriptions of Brownian motion still relied, up to very recently, on stochastic assumptions because the dynamics of the motion of the fluid atoms, which cause the Brownian motion of the heavier particles, was not introduced explicitly.

In recent years, various authors[2–4] have developed a microscopic theory of Brownian motion using the latest developments of non-equilibrium statistical mechanics. Since the laws of mechanics alone describe the irreversible behaviour of large systems (provided suitable initial conditions are chosen) no extramechanical assumptions are needed for a theory of Brownian motion.

Starting from the Liouville equation for the total distribution function, these authors derive a general transport equation for the one particle distribution function of the Brownian particle by integrating over the variables of the fluid molecules in certain limits involving the time scale and the size of the system. As the fluid is taken at thermal equilibrium the motion of the Brownian particle is studied under the *quasi-equilibrium condition*:

$$(\langle p_f^2 \rangle / \langle P^2 \rangle)^{\frac{1}{2}} \simeq (m/M)^{\frac{1}{2}} \equiv \gamma \ll 1 \tag{1}$$

which is obviously realized when both average momenta are in the thermal range (where P and p_f denote respectively the momentum of the Brownian particle and of the fluid molecule). The Fokker–Planck equation is then readily obtained as the limiting form of the Brownian particle generalized transport equation when γ tends to zero.

Very recently, some authors[5–10] have extended to quantum systems this method for obtaining a Fokker–Planck-like equation. The aim of the present paper is to give a general report of the study of the quantum-mechanical Brownian motion.

The quantum theory of Brownian motion appears to be useful in understanding various physical situations, for example theoretical interpretations of ionic mobilities in quantum liquids[8, 9, 14, 15] and predictions about non-classical isotope effects that should appear in diffusion experiments with heavy particles in quantum fluids at very low temperatures.[7] It should be therefore emphasized that limitations concerning the domain of validity of a Fokker–Planck-like description are necessary, chiefly in the very low temperature range where the zero-point motion of the particles plays an important part.

Here we shall apply the general theory of irreversible processes due to Prigogine and coworkers[11-13] by using for the description of quantum Brownian motion the method developed by Resibois and the author.[8, 9] Section 2 deals with the general formulation of the problem; we consider the model of one heavy charged Brownian particle (mass M, charge e) immersed in a fluid of N light quantum particles (for instance, bosons of mass m) and influenced by a weak electrostatic field E. Starting from the von Neumann equation for the $(N+1)$ particle density matrix, we obtain a generalized transport equation for the Brownian motion. From this equation we derive, in Section 3, the usual Fokker–Planck equation by expanding the dynamic properties of the Brownian particle in the mass ratio γ^2; the Fokker–Planck equation appearing then as the limiting form of the general transport equation when $\gamma \to 0$ [see Eq. (1)]. This requirement is obviously realized for a weakly coupled surrounding fluid such as a nearly perfect Bose gas. This model is then considered to interpret the experimental data obtained from measurements of ionic mobilities in liquid ^{4}He. In the next Section we discuss the problem of Brownian motion in a Fermi fluid where the convergence of the γ expansion appears to depend crucially on the temperature range considered; indeed it is shown that the condition of validity of the Fokker–Planck equation [Eq. (1)] should be replaced by the much more restrictive requirement:

$$(\langle p_i^2 \rangle / \langle P^2 \rangle)^{\frac{1}{2}} \simeq (m\varepsilon_F / MkT)^{\frac{1}{2}} \equiv \gamma\xi \ll 1 \qquad (2)$$

where ε_F denotes the Fermi energy and ξ is defined by $(\varepsilon_F/kT)^{\frac{1}{2}}$. To illustrate this case we give a theoretical interpretation of the behaviour of heavy ions in liquid ^{3}He.

Section 5 is devoted to the analysis of the next term of the

γ series appearing in the basic transport equation for Brownian motion. This examination of the first "correction" to the usual Fokker–Planck equation shows that condition (1) is no longer valid for strongly coupled systems (dense fluids) at very low temperatures, the zero-point motion of both kinds of particles starting to play a decisive part. Consequently when the localization effects are such that the convergence of the general transport equation is no longer ensured the whole framework of the usual Brownian motion theory breaks down.

Finally some lengthy calculations are reported in the Appendices.

The work reported in this paper has been carried out in the department of Professor I. Prigogine, at Brussels University. We wish to thank him for his continuous encouragement during its progress. We are also most indebted to P. Resibois, who suggested and collaborated in the major part of this work, and to H. T. Davis, who played an essential part in developing the results concerning the Fermi systems. Dr. J. Lekner read the manuscript and we thank him for his aid.

2. THE GENERALIZED TRANSPORT EQUATION FOR QUANTUM BROWNIAN MOTION

A. The Von Neumann–Liouville Equation

We consider a system enclosed in a box of volume Ω, made of one heavy charged particle (mass M, charge e) immersed in a fluid of N bosons of mass m ($m \ll M$), submitted to the influence of a weak external electrostatic field E. As in the equivalent classical situation[2-4] the motion of the heavy ion is studied under the quasi-equilibrium condition (1). This requirement can obviously be realized at sufficiently low temperatures for a *weakly coupled system* (at $T = 0$, $\langle p_1^2 \rangle = 0$!). However for a system with *strong interactions*, the zero-point motion of both kinds of particles starts to play a part; it is difficult then to make general assertions and Eq. (1) will in this case be considered as a sufficient condition for the validity of our proof. This point will be considered in more detail in Section 5. Let us stress also, that although the theory is formulated for bosons, the method is quite general provided that (1) is valid.

If we use a second quantization representation for free particles, we can cast the Hamiltonian of our system into the well-known

form:

$$H' = H + H^{e}; \quad H = H_0 + \lambda W \tag{3}$$

where the "internal" Hamiltonian H contains the kinetic energy term:*

$$H_0 = H_0^{B} + H_0^{f} = \frac{\hat{K}^2}{2M} + \sum_k \frac{k^2}{2} a_k^+ a_k \tag{4}$$

and the interaction energy between the particles:

$$\begin{aligned} \lambda W &= \lambda V^{f} + \lambda V^{fB} \\ &= \frac{\lambda}{2\Omega} \sum_{klpr} v(klpr)\, a_k^+ a_l^+ a_p a_r\, \delta^{Kr}(k+l-p-r) \\ &\quad + \frac{\lambda}{\Omega} \sum_{kl} u(k-l) \exp\left[-i(k-l)R\right] a_k^+ a_l \end{aligned} \tag{5}$$

where $(R, \hat{K})$ denote the coordinate and momentum operators of the Brownian particle; a_k^+ and a_k are the usual creation and destruction operators for bosons. Moreover $v(klpr)$ represents the fluid–fluid interaction while $u(k-l)$ corresponds to the potential energy between the fluid and the Brownian particle (both potentials are scaled with the dimensionless parameter λ). The eigenstates $|K\mathbf{n}\rangle$ of the unperturbed Hamiltonian in definition (3) are then given by

$$H_0 |K\mathbf{n}\rangle = \left(\frac{\hat{K}^2}{2M} + \sum_k \frac{k^2}{2} \hat{n}_k\right) |K\mathbf{n}\rangle \tag{6}$$

where $\mathbf{n}$ denotes the occupation numbers $(n_k, n_l, n_p, \ldots, n_r, \ldots)$.† Moreover H^{e} represents the interaction between the charged Brownian particle with the external electrostatic field

$$H^{e} = -eER \tag{7}$$

We start from the von Neumann equation for the total density matrix ρ, i.e. in the $|K\mathbf{n}\rangle$ representation:

$$i\partial_t \langle K\mathbf{n}|\rho|K'\mathbf{n}'\rangle = \langle K\mathbf{n}|[H', \rho]|K'\mathbf{n}'\rangle \tag{8}$$

* Except when explicitly noticed, we drop the vector notation and set $\mathbf{h} = m = 1$.

† As usual, we have for bosons:

$$a_k^+ |n_k\rangle = (n_k+1)^{\frac{1}{2}} |n_k+1\rangle, \quad a_k |n_k\rangle = n_k^{\frac{1}{2}} |n_k-1\rangle$$

We now rewrite this equation using the following definition valid for any operator A:[11,16]

$$\langle K\mathbf{n}|A|K'\mathbf{n}'\rangle \equiv A_{K-K',\mathbf{n}-\mathbf{n}'}\left(\frac{K+K'}{2},\frac{\mathbf{n}+\mathbf{n}'}{2}\right)\equiv A_{\kappa,\nu}(P,\mathbf{N}) \quad (9)$$

Here

$$\kappa = K-K', \quad P = \tfrac{1}{2}(K+K') \quad (10)$$

define a new set of variables for the Brownian particle, while for the fluid molecules we use

$$\nu = \mathbf{n}-\mathbf{n}', \quad \mathbf{N} = \tfrac{1}{2}(\mathbf{n}+\mathbf{n}') \quad (11)$$

with $\nu = (\nu_k, \nu_l, \nu_p, \ldots, \nu_r, \ldots)$ and $\mathbf{N} = (N_k, N_l, N_p, \ldots, N_r, \ldots)$. It is then easy to express Eq. (8) in terms of these variables; we obtain

$$\begin{aligned} &i\partial_t \rho_{\kappa,\nu}(P,\mathbf{N};t) \\ &= \sum_{\kappa',\nu'}\left[H'_{\kappa-\kappa',\nu-\nu'}\left(P+\frac{\kappa'}{2},\mathbf{N}+\frac{\nu'}{2}\right)\rho_{\nu'}\left(P+\frac{\kappa'-\kappa}{2},\mathbf{N}+\frac{\nu-\nu'}{2};t\right)\right. \\ &\quad \left. -H'_{\kappa-\kappa',\nu-\nu'}\left(P-\frac{\kappa'}{2},\mathbf{N}-\frac{\nu'}{2}\right)\rho_{\nu'}\left(P-\frac{\kappa'-\kappa}{2},\mathbf{N}-\frac{\nu'-\nu}{2};t\right)\right] \end{aligned} \quad (12)$$

where the summation over ν' runs over all possible values from $-N$ to N [that is for bosons: $\nu_k = n_k - n'_k$; ν_k in the range $(N, N-1, \ldots, -N+1, -N)$].

If we now introduce displacement operators $\zeta^{\pm\kappa}$, $\eta^{\pm\nu}$ such that for any function of P or $\mathbf{N}$:

$$\zeta^{\pm\kappa}\mathrm{f}(P) = \exp\left[\pm\frac{\kappa}{2}\frac{\partial}{\partial P}\right]\mathrm{f}(P) = \mathrm{f}\left(P\pm\frac{\kappa}{2}\right) \quad (13)$$

$$\eta^{\pm\nu}\mathrm{f}(\mathbf{N}) = \mathrm{f}\left(\mathbf{N}\pm\frac{\nu}{2}\right) \quad (14)$$

we can cast Eq. (8) into the following form:

$$i\partial_t \rho_{\kappa,\nu}(P,\mathbf{N};t) = \sum_{\kappa',\nu'}\langle\kappa\nu|\mathscr{H}'(P,\mathbf{N})|\kappa'\nu'\rangle\,\rho_{\kappa',\nu'}(P,\mathbf{N};t) \quad (15)$$

where the "von Neumann–Liouville operator"* $\mathscr{H}'$ is defined by

$$\begin{aligned} \langle\kappa\nu|\mathscr{H}'(P,\mathbf{N})|\kappa'\nu'\rangle = [&\zeta^{\kappa'}\eta^{\nu'}H'_{\kappa-\kappa',\nu-\nu'}(P,\mathbf{N})\,\zeta^{-\kappa}\eta^{-\nu} \\ &-\zeta^{-\kappa'}\eta^{-\nu'}H'_{\kappa-\kappa',\nu-\nu'}(P,\mathbf{N})\,\zeta^{\kappa}\eta^{\nu}] \end{aligned} \quad (16)$$

* Operators of this kind will be represented by script letters.

The $\rho_{\kappa\nu}(P, \mathbf{N})$ are the Fourier components of the Wigner distribution function of the whole system. The states $\kappa\nu \neq 0$ correspond to the existence of spatial correlations between the Brownian particle and the fluid; the dynamic evolution of these correlations is described by the von Neumann–Liouville equation (15). As in the case of quantum gases[16] Eq. (15) is the strict analogue of the classical Liouville equation. This great formal similarity will allow us to apply to this problem the general technique developed by Prigogine and coworkers[11–13, 16] to deal with non-equilibrium situations.

Before going to our derivation of a general transport equation for the Brownian particle momentum distribution function let us give the definitions of the script operators which correspond to the various terms of our starting Hamiltonian. Using definitions (9) and (16) with Eqs. (4), (5), and (7) we get after some elementary algebra:

$$\mathscr{H}' = \mathscr{H} + \mathscr{H}^{\mathrm{e}}; \quad \mathscr{H} = \mathscr{H}_0 + \lambda\mathscr{W} \tag{17}$$

where

$$\langle \kappa\nu | \mathscr{H}_0 | \kappa'\nu' \rangle = \langle \kappa\nu | \mathscr{H}_0^{\mathrm{B}} + \mathscr{H}_0^{\mathrm{f}} | \kappa'\nu' \rangle = [\kappa P/M + \boldsymbol{\epsilon}\cdot\nu]\, \delta^{\mathrm{Kr}}_{\kappa,\kappa'}\, \delta^{\mathrm{Kr}}_{\nu,\nu'} \tag{18}$$

represents the Brownian particle kinetic energy term plus the fluid unperturbed Hamiltonian (notice that $\boldsymbol{\epsilon}\cdot\nu$ means $\sum_k \varepsilon_k \nu_k$). On the other hand, the potential energy corresponds to

$$\langle \kappa\nu | \lambda\mathscr{W} | \kappa'\nu' \rangle = \langle \kappa\nu | \lambda\mathscr{V} + \lambda\mathscr{U} | \kappa'\nu' \rangle \tag{19}$$

where the "fluid–fluid" interaction term is given by

$$\begin{aligned} \langle \kappa\nu | \lambda\mathscr{V} | \kappa'\nu' \rangle = \frac{\lambda}{2\Omega} \sum_{klpr} v(klpr)\, \delta^{\mathrm{Kr}}(k+l-p-r) \\ \times \left[\prod_{klpr} \left(N_k + \frac{\nu'_k + 1}{2} \right)^{\frac{1}{2}} \eta^{-1_k - 1_l + 1_p + 1_r} \right. \\ \left. - \prod_{klpr} \left(N_k - \frac{\nu'_k - 1}{2} \right)^{\frac{1}{2}} \eta^{+1_k + 1_l - 1_p - 1_r} \right] \\ \times \prod_{k,l} \delta^{\mathrm{Kr}}_{\nu_k, \nu_k - 1} \prod_{p,r} \delta^{\mathrm{Kr}}_{\nu_p, \nu_p + 1}\, \delta^{\mathrm{Kr}}_{\{\nu\},\{\nu'\}}\, \delta^{\mathrm{Kr}}_{\kappa,\kappa'} \end{aligned} \tag{20}$$

and the "Brownian particle–fluid" interaction operator, defined by

$$\langle \kappa \nu | \lambda \mathscr{U} | \kappa' \nu' \rangle = \frac{\lambda}{\Omega} \sum_{kl} u(k-l)\, \delta^{\mathrm{Kr}}(k-l+\kappa-\kappa') \times \left[\prod_{k,l} \left(N_k + \frac{\nu'_k+1}{2} \right)^{\frac{1}{2}} \eta^{-1_k+1_l} \exp\left(\frac{\kappa'-\kappa}{2} \frac{\partial}{\partial P} \right) - \prod_{k,l} \left(N_k - \frac{\nu'_k-1}{2} \right)^{\frac{1}{2}} \eta^{+1_k-1_l} \exp\left(-\frac{\kappa'-\kappa}{2} \frac{\partial}{\partial P} \right) \right] \times \delta^{\mathrm{Kr}}_{\nu_k,\nu_k-1}\, \delta^{\mathrm{Kr}}_{\nu_l,\nu_l+1}\, \delta^{\mathrm{Kr}}_{\{\nu\},\{\nu'\}} \tag{21}$$

Finally the "external" Hamiltonian $\mathscr{H}^{\mathrm{e}}$ has the following form:

$$\langle \kappa \nu | \mathscr{H}^{\mathrm{e}} | \kappa' \nu' \rangle = \mathrm{i}e E \left[\frac{\partial}{\partial \left(P + \frac{\kappa}{2} \right)} \delta^{\mathrm{Kr}}_{\kappa,\kappa'} \exp\left(\frac{\kappa'-\kappa}{2} \frac{\partial}{\partial P} \right) - \frac{\partial}{\partial \left(P + \frac{\kappa}{2} - \kappa' \right)} \delta^{\mathrm{Kr}}_{\kappa,\kappa'} \exp\left(-\frac{\kappa'-\kappa}{2} \frac{\partial}{\partial P} \right) \right] \delta^{\mathrm{Kr}}_{\nu,\nu'} \tag{22}$$

B. The Master Equation in an External Electrostatic Field

We now analyse the evolution equation of the particle density matrix [Eq. (15)] in the special case where:

(1) the system is supposed to be uniform; we thus consider the evolution of the total momentum distribution function $\rho_0(P, \mathbf{N}; t)$;*

(2) the external electrostatic field E is switched on at the initial time. For $t \leqslant 0$, the system is at equilibrium:

$$\rho_{\kappa'\nu'}(P, \mathbf{N}; 0) = \rho^{\mathrm{eq}}_{\kappa'\nu'}(P, \mathbf{N})$$

(3) we suppose that this external field is weak and we limit ourselves to a *linear theory* in this smallness parameter.

We thus set:

$$\rho_0(P, \mathbf{N}; t) = \rho_0^{\mathrm{eq}}(P, \mathbf{N}) + \Delta\rho_0(P, \mathbf{N}; t)$$

* We shall often use the term "distribution function" in lieu of density matrix (recall how they are simply related in the definition of the Wigner distribution function).

the system being just off its equilibrium position under the influence of the weak external field.

In this case the von Neumann–Liouville equation [Eq. (15)] becomes

$$i\partial_t \rho_0(P, \mathbf{N}; t) = \sum_{\kappa'\nu'} \langle 0 | \mathscr{H}'(P, \mathbf{N}) | \kappa'\nu' \rangle \rho_{\kappa'\nu'}(P, \mathbf{N}; t) \qquad (23)$$

and its formal solution has the following form:

$$\rho_0(P, \mathbf{N}; t) = \sum_{\kappa'\nu'} \langle 0 | \exp[-i\mathscr{H}'(P, \mathbf{N})\, t] | \kappa'\nu' \rangle \rho^{eq}_{\kappa'\nu'}(P, \mathbf{N}) \qquad (24)$$

as may be checked by direct derivation. However, this expression is of no great help until we know how to operate explicitly with the very complicated exponential operator. In order to circumvent this difficulty, we shall use a resolvent technique: we define a resolvent operator $(\mathscr{H} - z)^{-1}$, a function of the complex variable z and write (see Résibois[13]):

$$\exp(-i\mathscr{H}' t) = -\frac{1}{2\pi i} \oint_C \frac{\exp(-izt)}{\mathscr{H}' - z}\, dz \qquad (25)$$

The contour C will always be chosen as a straight line parallel to the real axis in the upper half-plane and a large semi-circle in the lower half-plane: since $\mathscr{H}$ is Hermitian, all the singularities of the resolvant are on the real axis and are thus included in the contour C.

The resolvant technique furnishes a very elegant perturbation method for calculating Eq. (24), i.e.:

$$\rho_0(P, \mathbf{N}; t) = -\frac{1}{2\pi i} \oint_C dz \exp(-izt) \times \sum_{\kappa'\nu'} \langle 0 | (\mathscr{H}' - z)^{-1} | \kappa'\nu' \rangle \rho^{eq}_{\kappa'\nu'}(P, \mathbf{N}) \qquad (26)$$

Indeed, using the following formal expansion in the external force:

$$(\mathscr{H}' - z)^{-1} = (\mathscr{H} + \mathscr{H}^e - z)^{-1} = \sum_{n=0}^{8} (\mathscr{H} - z)^{-1} [-\mathscr{H}^e (\mathscr{H} - z)^{-1}]^n \qquad (27)$$

one sees immediately that, in a linear theory in the external

perturbation,* Eq. (26) may be cast into

$$\Delta\rho_0(P,\mathbf{N};t) = -\frac{1}{2\pi i}\oint_C \frac{dz}{z}\exp(-izt) \times \sum_{\kappa'\nu'} \langle 0|(\mathscr{H}-z)^{-1}\mathscr{H}^e|\kappa'\nu'\rangle \rho^{eq}_{\kappa'\nu'}(P,\mathbf{N}) \quad (28)$$

if one uses the obvious identity:

$$\mathscr{H}\rho^{eq} \equiv [H,\rho^{eq}] = 0 \quad (29)$$

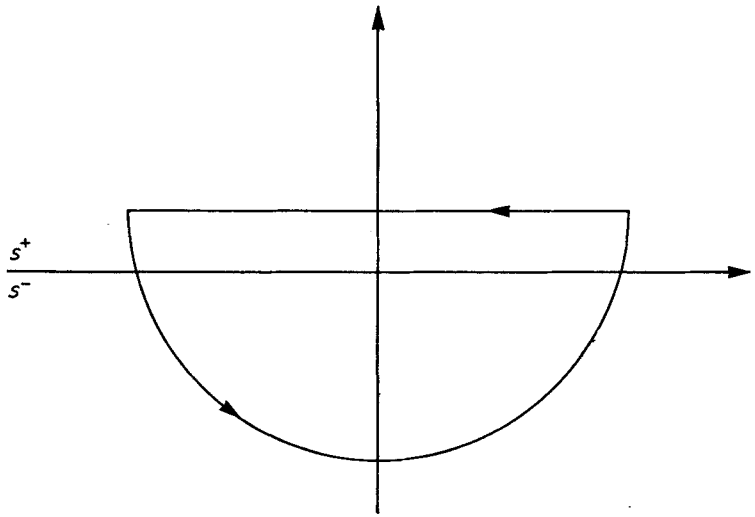

Fig. 1. The complex contour C in Eq. (25).

Moreover we may expand the right-hand side of Eq. (28) in the coupling constant λ, i.e. using the formal series (which is assumed to be convergent):

$$(\mathscr{H}-z)^{-1} = (\mathscr{H}_0-z)^{-1}\sum_{n=0}^{\infty}[-\lambda\mathscr{W}(\mathscr{H}_0-z)^{-1}]^n$$

Then we get

$$\Delta\rho_0(P,\mathbf{N};t) = -\frac{1}{2\pi i}\oint_C \frac{dz}{z}\exp(-izt) \times \sum_{\kappa'\nu'}\sum_{n=0}^{\infty}\langle 0|(1/-z)[-\lambda\mathscr{W}(\mathscr{H}_0-z)^{-1}]^n\mathscr{H}^e|\kappa'\nu'\rangle \rho^{eq}_{\kappa'\nu'}(P,\mathbf{N}) \quad (30)$$

* The external field is supposed weak and the series (27), convergent.

This expression describes the departure of the system from its equilibrium position under the influence of an external perturbation supposed weak. Here this deviation is expressed in terms of the spatial correlations existing between the Brownian particle and the fluid. In order to isolate in Eq. (30) the various contributions of physical interest let us introduce the following operators whose physical meaning will become clear.

We define the "diagonal fragment" $\Psi'_{00}(z)$ as the sum of all "irreducible" transitions leading from the state $|0\rangle$ to the same final state; by irreducible, we mean that all intermediate states $|\kappa\nu\rangle$ are such that $\kappa\nu \neq 0$ and this condition will be indicated by a dash ($'$) in all subsequent formulae. We thus have

$$\Psi'_{00}(z) = \sum_{n=2}^{\infty} \langle 0| -\lambda\mathscr{W}[(\mathscr{H}_0 - z)^{-1}(-\lambda\mathscr{W})]^{n-1}|0\rangle' \tag{31}$$

The "destruction term" is defined as the sum of all irreducible transitions starting from any initial state $|\kappa\nu\rangle$ with $\kappa\nu \neq 0$ and ending with the "vacuum" state $|0\rangle$:

$$\mathscr{D}_{0,\kappa\nu}(z) = \sum_{\kappa\nu} \sum_{n=1}^{\infty} \langle 0|[-\lambda\mathscr{W}(\mathscr{H}_0 - z)^{-1}]^n|\kappa\nu\rangle' \tag{32}$$

Finally in the calculation of the equilibrium correlation function $\rho^{eq}_{\kappa\nu}(P, \mathbf{N})$ we shall also need the so-called "creation fragment" which is defined by

$$\mathscr{C}_{\kappa\nu,0}(z) = \sum_{n=1}^{\infty} \langle \kappa\nu|[(\mathscr{H}_0 - z)^{-1}(-\lambda\mathscr{W})]^n|0\rangle' \tag{33}$$

If we now turn back to the perturbation expansion Eq. (30) for $\Delta\rho_0(P, \mathbf{N}; t)$, we may readily express the right-hand side as the sum of an arbitrary number of diagonal fragments preceded by a destruction term. We have identically:

$$\Delta\rho_0(P, \mathbf{N}; t) = -\frac{1}{2\pi i}\oint_C \frac{dz}{z} \exp(-izt) \sum_{\kappa'\nu'} \sum_{n=0}^{\infty} \frac{1}{-z}\left[\Psi'_{00}(z)\frac{1}{-z}\right]^n \times \{[\delta^{Kr}_{\kappa'\nu',0} + \mathscr{D}_{0,\kappa'\nu'}(z)][\mathscr{H}^e \rho^{eq}(P, \mathbf{N})]_{\kappa'\nu'}\} \tag{34}$$

$$\equiv \frac{1}{2\pi i}\oint_C \frac{dz}{z} \exp(-izt)[z + \Psi'_{00}(z)]^{-1} \times \{\mathscr{H}^e \rho^{eq}_0(P, \mathbf{N}) + \sum_{\kappa'\nu'} \mathscr{D}_{0,\kappa'\nu'}(z)[\mathscr{H}^e \rho^{eq}(P, \mathbf{N})]_{\kappa'\nu'}\} \tag{35}$$

where we have carried out the formal summation contained in Eq. (34).

To proceed with the discussion of Eq. (35) we need information concerning the analytic behaviour of the quantities $\Psi_{00}(z)$, $\mathscr{D}_{0,\kappa\nu}(z)$ or $\mathscr{C}_{\kappa\nu,0}(z)$ which will be all denoted formally by $F(z)$. We shall not discuss all the analytic properties of $F(z)$ in detail, but we shall simply give some important properties that may be deduced from complex analysis (for detailed justifications see references 11–13, 17).

$F(z)$ is an analytic function of z in the whole complex plane, except for a finite discontinuity along the real axis. As far as the destruction operator is concerned, this property is realized for a certain class of initial conditions, i.e. when the range of correlations in configuration space is finite. We have two functions $F^+(z)$ and $F^-(z)$ according to $\mathscr{I}m\, z > 0$ or $\mathscr{I}m\, z < 0$ which are analytic in their respective domains of definition, i.e. the first one in the upper half-plane S^+, the second one in the lower half-plane S^-. Moreover it is possible to show that $F^+(z)$ has an analytical continuation in the lower half-plane S^- and vice versa. This continuation has singularities which we shall always assume to be poles of finite order located at $z = z_i$ with the typical requirement:

$$\mathscr{I}m\, z_i = -\frac{1}{\tau_c} \tag{36}$$

where τ_c denotes the "collision time". This last property has been shown to be true for certain laws of interaction (for an explicit example see reference 13). In the following discussion Eq. (36) will be considered as a sufficient condition for the validity of the equations of evolution which we shall derive.

We first notice that because of the factor $\exp(-izt)$ the integral along the semi-circle at infinity is vanishing. We may thus formally replace $F(z)$ by $F^+(z)$ on that part of the contour. Moreover, along the real axis, we are in S^+, then we also need $F^+(z)$.

Second, as we are interested in the long time behaviour of the total momentum distribution function $\Delta\rho_0(P, \mathbf{N}; t)$, the integrations contained in Eq. (35) may be performed in the following asymptotic way:

$$I = \lim_{t\to\infty} \frac{1}{2\pi i} \oint_C \frac{\exp(-izt)}{z} F^+(z) \tag{37}$$

and then readily evaluated using the well-known residue theorem:

$$I = \lim_{t\to\infty}\left[F^{+}(0) + \sum_{z=z_i} \frac{\exp(-iz_i t)}{z_i} \operatorname{Res} F(z)\big|_{z=z_i}\right] \tag{38}$$

$$I = F^{+}(0) \tag{39}$$

Notice that as $F^{+}(z)$ is defined in S^{+}, the residue we denote simply $F^{+}(0)$ taken in the limit $z\to 0^{+}$ or $z\to i0$. Consequently the stationary momentum distribution function $\Delta\rho_0(P,\mathbf{N})$, which is realized after a long time when the system is submitted to a weak external electrostatic field, is given by the solution of the following time-independent transport equation:

$$i\Psi^{+}_{00}(0)\,\Delta\rho_0(P,\mathbf{N}) = i\mathscr{H}^{e}\,\rho_0^{eq}(P,\mathbf{N}) + i\sum_{\kappa'\nu'}\mathscr{D}^{+}_{0,\kappa'\nu'}(0)\,[\mathscr{H}^{e}\,\rho^{eq}(P,\mathbf{N})]_{\kappa'\nu'} \tag{40}$$

Before explaining the physical meaning of the different terms of this transport equation, let us quote a useful relation between the equilibrium correlations ($\kappa\nu\neq 0$) and the momentum distribution function ($\kappa\nu = 0$). One can show that

$$\rho^{eq}_{\kappa\nu}(P,\mathbf{N}) = \lim_{t\to\infty}\rho_{\kappa\nu}(P,\mathbf{N};\,t) \equiv \mathscr{C}^{+}_{\kappa\nu,0}(0)\,\rho_0^{eq}(P,\mathbf{N}) \tag{41}$$

where the creation term $\mathscr{C}_{\kappa\nu,0}(z)$ is defined by Eq. (33). We do not wish to give a detailed proof of Eq. (41) here (see, for instance, reference 13); let us merely point out the fact that this dynamic formulation of the equilibrium correlations leads to results analogous to the usual methods based on the canonical distribution:

$$\rho^{eq}_{\kappa\nu}(P,\mathbf{N}) = \left[\frac{\exp(-\beta H)}{\operatorname{Tr}\exp(-\beta H)}\right]_{\kappa\nu} \tag{42}$$

but it has the advantage of being readily extended to non-equilibrium situations.

With Eq. (41) the basic transport equation (40) may be cast into the compact form:

$$i\Psi^{+}_{00}(0)\,\Delta\rho_0(P,\mathbf{N}) = i\mathscr{H}^{e}\,\rho_0^{eq}(P,\mathbf{N}) + i\sum_{\kappa'\nu'}\mathscr{D}^{+}_{0,\kappa'\nu'}(0)\,\mathscr{H}^{e}\,\mathscr{C}_{\kappa'\nu',0}(0)\,\rho_0^{eq}(P,\mathbf{N}) \tag{43}$$

This equation describes exactly the linear response of the system to an external electrostatic field in the limit $t\to\infty$ and with

equilibrium initial conditions. Bearing in mind that in this stationary situation one has

$$\partial_t \rho_0(P, \mathbf{N}; t) = \partial_t \rho_0(P, \mathbf{N}; t)|_{\text{coll}} + \partial_t \rho_0(P, \mathbf{N}; t)|_{\text{field}} \equiv 0$$

one may easily point out the physical meaning of the different terms of Eq. (43). The left-hand side contains the asymptotic collision operator which generalizes to a strongly coupled system the well-known quantum-mechanical collision Boltzmann operator for a dilute system. The first term of the right-hand side, where the external field acts on a "vacuum" state $|0\rangle$, is the usual flow term coming from the influence of the external perturbation on the momentum distribution function of the system. The second term corresponds to situations where the outer force acts on particles which are mutually interacting; in this sense, it represents the effect of the external field *during* the collision process. In the dilute gas limit, this effect disappears because the duration of the collision is very small. However, in a dense system, it can play an essential part.

It should be emphasized that because we are interested in a linear transport theory, the operators of the right-hand side of Eq. (43) are acting on the exact equilibrium distribution function which may "formally" be factorized:*

$$\rho_0^{\text{eq}}(P, \mathbf{N}) = \phi_0(\gamma; P)\, \rho_0^{\text{f}}(\mathbf{N}) \tag{44}$$

where $\phi_0(\gamma; P)$ is the complete quantum equilibrium distribution function of the Brownian particle which still depends on γ [because of the non-commutativity of H_0^{B} and $H^{\text{f}} = H_0^{\text{f}} + \lambda W$, see Eqs. (4) and (5)] and $\rho_0^{\text{f}}(\mathbf{N})$ denotes the equilibrium distribution function of the fluid particles.

Now we shall show that, although Eq. (43) is still purely formal—in the sense that it involves the complete N particle distribution function $\Delta\rho_0(P, \mathbf{N})$—it can be reduced to a transport equation for the single Brownian particle distribution function.

* By "formally" we mean the following: in the presence of interactions there is of course no strict factorization of the density matrix Eq. (44). However, if we compute an average value and denote $\langle\phi(P)\rangle$ the momentum distribution of the heavy particle while $\langle n_k\rangle = \text{Tr}\, \hat{n}_k\, \rho^{\text{f}}$, it may be shown that

$$\langle\phi(P)\, n_k\rangle = \langle\phi(P)\rangle\, \langle n_k\rangle + O(N^{-1})$$

(see reference 4 for a similar argument).

C. The Transport Equation for Quantum Brownian Motion

We assume that the departure from equilibrium may be written in the linear form:

$$\Delta\rho_0(P,\mathbf{N}) = \rho_0^{\mathrm{f}}(\mathbf{N})\,\delta\phi(P) + \phi_0(\gamma;\,P)\,\delta\rho^{\mathrm{f}}(\mathbf{N}) \tag{45}$$

The justification of this assumption of molecular chaos is now well established in the limit of an infinite system ($N\to\infty, \Omega\to\infty$; $N/\Omega = \rho$ = finite) and we shall not discuss it here.

Let us now recall the main feature of our Brownian motion model, which is that when *a very few* heavy particles move through a fluid of N light particles they cannot cause it to depart from its equilibrium condition, the non-equilibrium situation of the Brownian particles being caused by an external perturbation. Thus, in our case, if we allow that the fluid particles are not affected by the presence of the Brownian particle we can set in Eq. (45):

$$\delta\rho^{\mathrm{f}}(\mathbf{N}) = 0 \tag{46}$$

Let us also note that this rather obvious statement can be supported with a mathematical demonstration valid up to order $O(N^{-1})$ (see, for instance, reference 2).

Inserting Eqs. (44) and (45) into Eq. (43) and summing over the fluid variables $\mathbf{N}$, one can reduce the formal equation (43) to the following closed transport equation for the Brownian particle distribution function:

$$\langle\Psi_{00}^{+}(0)\rangle_{\mathrm{f}}\,\delta\phi(P) = [\mathscr{H}^{\mathrm{e}} + \langle\sum_{\kappa'\nu'}\mathscr{D}_{0,\kappa'\nu'}^{+}(0)\,\mathscr{H}^{\mathrm{e}}\,\mathscr{C}_{\kappa'\nu',0}^{+}(0)\rangle_{\mathrm{f}}]\,\phi_0(\gamma;\,P) \tag{47}$$

where we have averaged the various operator quantities in the variables P and $\mathbf{N}$ over the fluid equilibrium distribution function ρ^{f} (where Z_{f} denotes the fluid partition function):

$$\rho^{\mathrm{f}} = Z_{\mathrm{f}}^{-1}\exp(-\beta H^{\mathrm{f}}); \quad H^{\mathrm{f}} = H_0^{\mathrm{f}} + V^{\mathrm{f}} + V^{\mathrm{fB}} \tag{48}$$

using the definition

$$\langle A\rangle_{\mathrm{f}} = \mathrm{Tr}\,A\rho_{\mathrm{f}} = \sum_{\mathbf{N}} A(\mathbf{N})\,\rho_0^{\mathrm{f}}(\mathbf{N}) \tag{49}$$

The generalized transport equation for quantum Brownian motion, Eq. (47), will be the starting point of: (1) a microscopic derivation of the usual Fokker–Planck equation (Section 3) and (2) discussion of the validity of a Fokker–Planck type description for a Brownian motion situation in the very low temperature limit (Section 4).

D. Expansion in the Momentum Ratio

In the basic transport equation (47) we now take into account explicitly the Brownian motion condition (1). Let us first introduce a reduced variable

$$p = \gamma P \tag{50}$$

defined in such a way that if the "classical requirement" (1) is satisfied, the average value of p remains finite in the limit $\gamma \to 0$. This new variable enables us to take out the γ-dependence of the "von Neumann–Liouville" operators [see Eqs. (17)–(22)] and split them into

$$\mathscr{H} = \mathscr{H}^{\mathrm{f}} + \gamma \mathscr{H}^{\mathrm{I}} + \gamma^2 \mathscr{H}^{\mathrm{II}} + \gamma^3 \mathscr{H}^{\mathrm{III}} + O(\gamma^4) \tag{51}$$

$$\mathscr{H}_0 = \mathscr{H}_0^{\mathrm{f}} + \gamma \mathscr{H}_0^{\mathrm{I}} \tag{52}$$

$$\mathscr{W} = \mathscr{V}^{\mathrm{f}} + \gamma \mathscr{U}^{\mathrm{I}} + \gamma^2 \mathscr{U}^{\mathrm{II}} + \gamma^3 \mathscr{U}^{\mathrm{III}} + O(\gamma^4) \tag{53}$$

We have thus, parallel to the classical case:

$$\mathscr{H}_0^{\mathrm{f}} = \boldsymbol{\epsilon} \cdot \boldsymbol{\nu} \tag{54}$$

(fluid unperturbed von Nuemann–Liouville operator)

$$\gamma \mathscr{H}_0^{\mathrm{I}} = \mathscr{H}_0^{\mathrm{B}} = \gamma \hat{\kappa} p \tag{55}$$

(Brownian particle unperturbed von Neumann–Liouville operator). Here $\hat{\kappa}$ is an operator defined by $\hat{\kappa} | \kappa \boldsymbol{\nu} \rangle = \kappa | \kappa \boldsymbol{\nu} \rangle$ [see Eq. (18)]. Moreover,

$$\mathscr{V}^{\mathrm{f}} = \mathscr{V} + \mathscr{U}^{(0)} \tag{56}$$

(perturbation that the fluid would feel if the Brownian particle was fixed). Here $\mathscr{V}$ is given by Eq. (20) and $\mathscr{U}^{(0)}$ is zero-order in γ of the expression (21) where we simply replace the displacement operators $\zeta^{\pm\kappa}$ by the γ-expansion:

$$\zeta^{\pm\kappa} = \sum_{n=0}^{\infty} \frac{1}{n!} \left(\pm \tfrac{1}{2} \gamma \kappa \frac{\partial}{\partial p} \right)$$

Similarly, at order γ, the interaction of the Brownian particle with the fluid corresponds to

$$\begin{aligned} &\langle \kappa \boldsymbol{\nu} | \gamma \mathscr{U}^{\mathrm{I}} | \kappa' \boldsymbol{\nu}' \rangle \\ &\quad = \lambda \Omega^{-1} \sum_{k,l} u(k-l)\, \delta^{\mathrm{Kr}}(k-l+\kappa-\kappa') \{ [(N_k + \tfrac{1}{2}\nu_k)(N_l + \tfrac{1}{2}\nu_l + 1)]^{\frac{1}{2}} \\ &\qquad \times \eta^{-1_k+1_l} + [(N_k - \tfrac{1}{2}\nu_k + 1)(N_l - \tfrac{1}{2}\nu_l)]^{\frac{1}{2}} \eta^{+1_k-1_l} \} \\ &\qquad \times \tfrac{1}{2} \gamma (k-l) \frac{\partial}{\partial p} \delta^{\mathrm{Kr}}_{\nu_k, \nu_{k'}+1} \delta^{\mathrm{Kr}}_{\nu_l, \nu_{l'}-1} \delta^{\mathrm{Kr}}_{\{\nu\}, \{\nu'\}}, \end{aligned} \tag{57}$$

Let us here explain the meaning of this expression. Let us express how this operator acts on any quantity $A(\mathbf{n})$ which we choose, for simplicity, diagonal in the occupation number $\mathbf{n}$:

$$\begin{aligned}\langle\kappa\nu|\gamma\mathscr{U}^{\mathrm{I}}|\kappa'0\rangle A_0(\mathbf{N}) &= \lambda\Omega^{-1}\sum_{k,l} u(k-l)\,\delta(k-l+\kappa-\kappa')\,\tfrac{1}{2}\gamma(k-l)\frac{\partial}{\partial p}\delta^{\mathrm{Kr}}_{\nu_k,1}\delta^{\mathrm{Kr}}_{\nu_l,-1}\delta^{\mathrm{Kr}}_{\{\nu\}',0}\\ &\quad\times[(N_k+\tfrac{1}{2})(N_l+\tfrac{1}{2})]^{\frac{1}{2}}[A_0(N_k-\tfrac{1}{2},N_l+\tfrac{1}{2},\{N\}')\\ &\quad-A_0(N_k+\tfrac{1}{2},N_l-\tfrac{1}{2},\{N\}')]\end{aligned}$$

If we now go back to the usual occupation number representation ($\mathbf{n}=\mathbf{N}+\frac{1}{2}\boldsymbol{\nu}$) we may write

$$\begin{aligned}\langle\kappa\nu|\gamma\mathscr{U}^{\mathrm{I}}|\kappa'0\rangle A_0(\mathbf{N}) &= \lambda\Omega^{-1}\sum_{k,l} u(k-l)\,\delta(k-l+\kappa-\kappa')\,\tfrac{1}{2}\gamma(k-l)\frac{\partial}{\partial p}\delta^{\mathrm{Kr}}_{\nu_k,1}\delta^{\mathrm{Kr}}_{\nu_l,-1}\delta_{\{\nu\}',0}\\ &\quad\times[n_k(n_l+1)]^{\frac{1}{2}}[\langle n_k-1,n_l+1,\{n\}'|A|n_k-1,n_l+1,\{n\}'\rangle\\ &\quad-\langle\mathbf{n}|A|\mathbf{n}\rangle]\end{aligned}$$

or, with the definition of the operators a_k^+, a_k:

$$\begin{aligned}\langle\kappa\nu|\gamma\mathscr{U}^{\mathrm{I}}|\kappa'0\rangle A_0(\mathbf{N}) &= \lambda\Omega^{-1}\sum_{k,l} u(k-l)\,\delta(k-l+\kappa-\kappa')\,\tfrac{1}{2}\gamma(k-l)\frac{\partial}{\partial p}\delta^{\mathrm{Kr}}_{\nu_k,1}\delta^{\mathrm{Kr}}_{\nu_l,-1}\delta^{\mathrm{Kr}}_{\{\nu\}',0}\\ &\quad\times\langle\mathbf{n}|a_k a_l^+ A + A a_k^+ a_l|n_k-1,n_l+1,\{n\}'\rangle\end{aligned}$$

This example shows that the operator $\gamma\mathscr{U}^{\mathrm{I}}$ may be represented as

$$\gamma\mathscr{U}^{\mathrm{I}} = \gamma\mathscr{F}^+\frac{\partial}{\partial p} \tag{58}$$

where $\mathscr{F}^+$ is an operator associated with the quantum-mechanical force F existing between the Brownian particle and the fluid, the subscript $(+)$ having been introduced as a reminder that it corresponds to an anticommutator, i.e.:

$$\mathscr{F}^+\mathscr{A}\to\frac{\mathrm{i}}{2}[\hat{F}A+A\hat{F}] \tag{59}$$

with

$$\hat{F} = \mathrm{i}\lambda\Omega^{-1}\sum_k q u(q)\,a_k^+ a_{k-q} = \mathrm{i}[\hat{\kappa}, V^{\mathrm{fB}}] \tag{60}$$

Let us add that the terms of $\mathscr{H}^{\mathrm{II}}$ (of order γ^2) can be obtained in a similar fashion but we shall not need their explicit form here.

If we note that $\mathscr{H}^{\mathrm{e}}$, as given by Eq. (22), is also of order γ we may easily obtain the following expansions:

$$\langle \Psi^{+}_{00}(\gamma^{-1}p, N; 0)\rangle_{\mathrm{f}} = \sum_{n=\mathrm{i}}^{\infty} \gamma^{2n}\, \Omega^{(2n)} \tag{61}$$

$$\langle \sum_{\kappa\nu} \mathscr{D}^{+}_{0,\kappa\nu}(\gamma^{-1}p, N; 0)\, \gamma \mathscr{H}^{\mathrm{e}}\, \mathscr{C}^{+}_{\kappa\nu,0}(\gamma^{-1}p, N; 0)\rangle_{\mathrm{f}} = \sum_{n=3}^{\infty} \gamma^{n}\, G^{(n)} \tag{62}$$

From the symmetry properties of these expressions, one can show that

$$\Omega^{(0)} = \Omega^{(2n+1)} = 0 \tag{63a}$$

$$G^{(1)} = G^{(2)} = 0 \tag{63b}$$

For instance, by examining the explicit form of $\Omega^{(0)}$ one sees immediately that this contribution vanishes identically once the trace over the fluid variables is taken, indeed we have

$$\sum_{\mathbf{N}} (\eta^{\nu} - \eta^{-\nu})\, \mathrm{f}(\mathbf{N}) \equiv 0 \tag{64}$$

Moreover let us stress that in Eq. (47) the complete equilibrium distribution function of the Brownian particle is involved; it can itself be expanded in γ:

$$\phi_0(\gamma; P) = \sum_{n=0}^{\infty} \gamma^{n}\, \phi_0^{(n)}(p) \tag{65}$$

However, as is easily checked, the zero-order term of the Brownian particle equilibrium distribution function is simply the unperturbed Maxwellian distribution function

$$\phi_0^{(0)}(P) \equiv \left(\frac{M\beta}{2\pi}\right)^{\frac{3}{2}} \exp\left(-\frac{\beta P^2}{2M}\right) \tag{66}$$

and the higher order terms express quantum deviations (which may however become large in the low temperature limit, see Section 4.B).

When relations Eqs. (61), (62), and (65) are introduced in our basic transport equation Eq. (47), we obtain

$$\begin{aligned} &\mathrm{i}[\gamma \mathscr{H}^{\mathrm{e}} + (\gamma^3 G^{(3)} + \gamma^4 G^{(4)} + \ldots)]\, [\phi_0^{(0)}(P) + \gamma^2 \phi_0^{(2)}(P) + \ldots] \\ &\quad = \mathrm{i}(\gamma^2 \Omega^{(2)} + \gamma^4 \Omega^{(4)} + \ldots)\, \phi(P) \end{aligned} \tag{67}$$

where we have turned back to the ordinary momentum variable P.