

## Microscopic Theory of Brownian Motion: The Multiple-Time-Scale Point of View\*

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We present a microscopic derivation of a Fokker-Planck equation for the distribution function of a heavy Brownian particle in a dense fluid from the Liouville equation. The usual perturbation theory suffers from the presence of secular terms familiar from non-linear mechanics. We employ the "multiple time scale" technique developed by Frieman and Sandri to eliminate the secular terms and render the expansions uniformly valid in time. The method introduces explicit time variables to exploit the existence of a multiplicity of time scales inherent in the problem. Using this formalism we derive the Fokker-Planck equation for spatially inhomogeneous Brownian motion.

### I. INTRODUCTION

In the past several years there has been considerable interest in the microscopic justification of Brownian Motion theory. The central aim is to derive from molecular considerations a transport equation for the Brownian particle distribution function  $\Psi(\vec{R}, \vec{P}, t)$ . From stochastic considerations one expects the transport equation to be a Fokker-Planck equation of the form:

$$\frac{\partial \Psi}{\partial t} = - (\vec{P}/M) \cdot \nabla_{\vec{R}} \Psi + \zeta \nabla_{\vec{P}} \cdot [\vec{P} + (M/\beta) \nabla_{\vec{P}}] \Psi. \quad (1.1)$$

In *dense* fluid systems this problem is usually cast in terms of describing the effect of bath particles of mass  $m$  on the Brownian particle of mass  $M$  in the limit where  $M \gg m$ .

The first rigorous analysis of this problem appears to be due to Lebowitz and Rubin,<sup>1</sup> Beginning with the Liouville equation for the distribution function  $f$  of the entire system they arrive at Eq. (1.1) by expanding dynamical properties of the Brownian particle in the mass ratio  $\gamma^2 = m/M$ . Subsequently Lebowitz and Résibois,<sup>2</sup> employing projection-operator techniques developed by Zwanzig,<sup>3</sup> extended the analysis to include the effects of a (small) external, oscillating field acting on the Brownian particle. Lebowitz and Résibois also demonstrate the equivalence of their results with earlier work by Résibois and Davis<sup>4</sup> that employed the Prigogine-Résibois formalism. Finally we mention a recent unpublished investigation by Oppenheim and Mazur<sup>5</sup> that examines in somewhat greater detail the justification for the limiting procedure required by the projection-operator technique.

The purpose of this article is to develop microscopic Brownian motion theory by the multiple-time-scale method. This method has its origin in the field of nonlinear mechanics.<sup>6</sup> The method has been extensively employed, most notably by Frieman<sup>7</sup> and Sandri,<sup>8</sup> to obtain kinetic equations for dilute gases and plasmas. Since several summaries of the method are available in the literature,<sup>9-11</sup> a detailed exposition of the technique will not be included here.

We mention in passing that Frieman<sup>7</sup> and later Su<sup>9</sup> used the multiple-time-scale method to obtain kinetic equations for reduced distribution functions

in *weakly interacting* fluid systems. They obtain a so-called Fokker-Planck equation for the one-particle distribution function. This equation is nonlinear and hence differs from Eq. (1.1). The difference arises because in the weakly interacting case the parameter of smallness is (mean potential energy/ $kT$ ) while in the heavy mass case the parameter of smallness is  $\gamma^2 = m/M$ .

Our motivation for presenting this alternative derivation of the transport equation for the Brownian particle Eq. (1.1) is based on the conviction that the multiple-time-scale method provides considerable advantage in displaying the physics of the relaxation process. The validity of the expansion procedures employed in Refs. 1 and 2 depends on the fact that the ratio of the average thermal speed of the Brownian particle to a bath particle is of order  $\gamma$ . Hence it takes the Brownian particle  $\gamma^{-1}$  times longer than a bath particle to traverse a unit length. One may conclude that the time scale on which the Brownian particle distribution function varies is "slow" compared to the time scale on which the bath distribution function varies. The virtue of the multiple-time-scale method is that it focuses attention, at the outset, on the existence of the different time scales in the problem. Zwanzig has emphasized<sup>12</sup> that the type of expansion procedures employed in Refs. 1 and 2 can only be valid in the limit of "slow" processes.

### II. GENERAL FORMULATION

The Hamiltonian of our classical system consisting of  $N$  bath particles and a Brownian particle is

$$H = H_p + H_0 + U = H_p + H_b, \quad (2.1)$$

where  $H_p = P^2/2M$  is the kinetic energy of the Brownian particle,  $H_0$  is the Hamiltonian for the isolated bath,

$$H_0 = \sum_{i=1}^N \frac{p_i^2}{2m} + \sum_{i < j} \phi(r_{ij}), \quad (2.2)$$

and  $U$  is the potential energy of interaction between the Brownian particle and the bath particles,

$$U = \sum_{i=1}^N u(|\vec{r}_i - \vec{R}|). \quad (2.3)$$

We assume that the entire system is enclosed in a volume  $V$  which is in thermal contact with the surroundings at temperature  $T$ .

The distribution function for the entire system  $f(t) = f(\vec{r}^N, \vec{p}^N; \vec{R}, \vec{P}; t)$  obeys the Liouville equation

$$\partial f / \partial t = -iL f(t), \quad (2.4)$$

where  $iL = iL_b + iL'$ ,

$$iL_b = \sum_{i=1}^N \left( \frac{p_i}{m} \cdot \nabla_{\vec{r}_i} - \nabla_{\vec{r}_i} \cdot u(|\vec{r}_i - \vec{R}|) \cdot \nabla_{\vec{p}_i} - \sum_{j \neq i} \nabla_{\vec{r}_i} \cdot \phi(r_{ij}) \cdot \nabla_{\vec{p}_i} \right), \quad (2.5)$$

and

$$iL' = (\vec{P}/M) \cdot \nabla_{\vec{R}} - \nabla_{\vec{R}} U \cdot \nabla_{\vec{P}}. \quad (2.6)$$

Note that  $L_b$  and  $H_b$  still contain coupling between the fluid and the Brownian particles.

We now perform the change of variables  $\hat{\vec{P}} = \gamma \vec{P}$  and transform  $iL'$  into

$$iL' = i\gamma \hat{L}' = \gamma \left[ (\hat{\vec{P}}/m) \cdot \nabla_{\vec{R}} - \nabla_{\vec{R}} U \cdot \nabla_{\hat{\vec{P}}} \right]. \quad (2.7)$$

Our analysis will take place in terms of the variable  $\hat{\vec{P}}$ . For ease of notation, however, we suppress the caret.

The definition of the Brownian particle distribution function is

$$\Psi(t) = \Psi(\vec{R}, \vec{P}; t) = \int f(\vec{r}^N, \vec{p}^N; \vec{R}, \vec{P}; t) d\vec{r}^N d\vec{p}^N. \quad (2.8)$$

Integration of Eq. (2.4) over  $\vec{r}^N$  and  $\vec{p}^N$  yields the equation of motion for  $\Psi$

$$i \frac{\partial \Psi}{\partial t} = -i\gamma \frac{\vec{P}}{m} \cdot \nabla_{\vec{R}} \Psi + i\gamma \mathcal{L}[f], \quad (2.9)$$

where the operator  $i\mathcal{L}$  is defined by

$$i\mathcal{L}[A] = i \int (\nabla_{\vec{R}} U) \cdot \nabla_{\vec{P}} A d\vec{r}^N d\vec{p}^N. \quad (2.10)$$

We now begin the multiple-time-scale analysis by replacing the single time variable of  $f(t)$  and  $\Psi(t)$  by a set of time variables  $\tau_0, \tau_1, \tau_2, \dots$  each of which is treated as an independent variable. Thus

$$f(t) = f(\tau_0, \tau_1, \dots, \tau_n), \quad (2.11)$$

$$\text{and } \Psi(t) = \Psi(\tau_0, \tau_1, \dots, \tau_n). \quad (2.12)$$

We seek a series solutions of Eqs. (2.4) and (2.9) of the form

$$f = f_0 + \gamma f_1 + \gamma^2 f_2 + \dots, \quad (2.13)$$

$$\text{and } \Psi = \Psi_0 + \gamma \Psi_1 + \gamma^2 \Psi_2 + \dots. \quad (2.14)$$

Within the framework of the multiple-time-scale method one asserts that the new time variables  $\{\tau_n\}$  are related to the real time  $t$  by the simple relation

$$\tau_n = \gamma^n t. \quad (2.15)$$

The time derivative is also formally expanded in powers of  $\gamma$ ,

$$\frac{\partial}{\partial t} = \frac{\partial}{\partial \tau_0} + \gamma \frac{\partial}{\partial \tau_1} + \gamma^2 \frac{\partial}{\partial \tau_2} + \dots. \quad (2.16)$$

Note that at the outset explicit recognition is given to the possibility that the system evolves on various time scales.

Our next step is to substitute Eqs. (2.13), (2.14), and (2.16) into Eqs. (2.4) and (2.9). If one equates the coefficients of successive powers of  $\gamma$  one obtains from Eq. (2.4) the set of equations (to order  $\gamma^2$ ):

$$i \frac{\partial f_0}{\partial \tau_0} = L_b f_0, \quad (2.17)$$

$$i \left( \frac{\partial f_1}{\partial \tau_0} + \frac{\partial f_0}{\partial \tau_1} \right) = L_b f_1 + L' f_0, \quad (2.18)$$

$$i \left( \frac{\partial f_2}{\partial \tau_0} + \frac{\partial f_1}{\partial \tau_1} + \frac{\partial f_0}{\partial \tau_2} \right) = L_b f_2 + L' f_1. \quad (2.19)$$

From Eq. (2.9) for  $\Psi(t)$  one obtains the set (to order  $\gamma^2$ ):

$$i \frac{\partial \Psi_0}{\partial \tau_0} = 0, \quad (2.20)$$

$$i \left( \frac{\partial \Psi_1}{\partial \tau_0} + \frac{\partial \Psi_0}{\partial \tau_1} \right) = -i \frac{\vec{P}}{m} \cdot \nabla_{\vec{R}} \Psi_0 + i\mathcal{L}[f_0], \quad (2.21)$$

$$i \left( \frac{\partial \Psi_2}{\partial \tau_0} + \frac{\partial \Psi_1}{\partial \tau_1} + \frac{\partial \Psi_0}{\partial \tau_2} \right) = -i \frac{\vec{P}}{m} \cdot \nabla_{\vec{R}} \Psi_1 + i\mathcal{L}[f_1]. \quad (2.22)$$

We must now solve the set of Eqs. (2.17)–(2.22) subject to appropriate initial conditions. The heart of the multiple-time-scale method is the proviso that the increased flexibility which accompanies the extended definition of the functions may be used to eliminate secular behavior whenever it occurs.

### III. BOUNDARY CONDITIONS

The formulation of appropriate initial conditions for the extended functions Eqs. (2.13) and (2.14)

is an important part of the multiple-time-scale method. In general the complete distribution function  $f$  and the Brownian particle distribution function  $\Psi$  are related by

$$f(\vec{r}^N, \vec{p}^N, \vec{R}, \vec{P}; t) = h(\vec{r}^N, \vec{p}^N; t/\vec{R}, \vec{P}; t) \Psi(\vec{R}, \vec{P}; t), \quad (3.1)$$

where  $h$  is the conditional distribution function of finding the bath in the neighborhood of the phase point  $(\vec{r}^N, \vec{p}^N)$  at time  $t$  given that the Brownian particle is in the neighborhood of  $(\vec{R}, \vec{P})$  at time  $t$ . We assume that at  $t=0$   $h$  has its equilibrium value,

$$h(\vec{r}^N, \vec{p}^N; 0/\vec{R}, \vec{P}; 0) = Z^{-1} \exp(-\beta H_b) \equiv h_{\text{eq}}, \quad (3.2)$$

$$\text{where } Z = \int \exp(-\beta H_b) d\vec{r}^N d\vec{p}^N. \quad (3.3)$$

In terms of the extended functions the initial condition is

$$f(0, \tau_1, \dots, \tau_n) = h_{\text{eq}} \Psi(0, \tau_1, \dots, \tau_n). \quad (3.4)$$

It is possible to choose

$$\Psi(0, \tau_1, \dots, \tau_n) = \Psi_0(0, \tau_1, \dots, \tau_n),$$

$$\text{and } \Psi_n(0, \tau_1, \dots, \tau_n) = 0 \quad n \geq 1, \quad (3.5)$$

from which it follows that

$$\begin{aligned} f_0(0, \tau_1, \dots, \tau_n) &= h_{\text{eq}} \Psi_0(0, \tau_1, \dots, \tau_n) \\ &= h_{\text{eq}} \Psi(0, \tau_1, \dots, \tau_n) \\ &= f(0, \tau_1, \dots, \tau_n) \end{aligned} \quad (3.6)$$

$$\text{and } f_n(0, \tau_1, \dots, \tau_n) = 0, \quad n \geq 1. \quad (3.7)$$

The initial condition we have assumed, Eq. (3.2), corresponds to assuming that at  $t=0$  the bath particles have established equilibrium with respect to the potential  $U$ . The initial nonequilibrium distribution for the Brownian particle may be visualized as having been established by an external disturbance that was present for  $t < 0$ , and is abruptly removed at  $t=0$ .

With this formulation of the initial conditions we are in a position to solve the set of Eqs. (2.17)–(2.22).

#### IV. THE SPATIALLY UNIFORM CASE

From Eq. (2.20) it follows that  $\Psi_0$  maintains its initial value on the  $\tau_0$  scale and hence

$$\Psi_0 = \Psi_0(\tau_1, \dots, \tau_n). \quad (4.1)$$

From Eq. (2.17) it follows that

$$f_0(\tau_0, \tau_1, \dots, \tau_n) = e^{-iL_b \tau_0} f_0(0, \tau_1, \dots, \tau_n). \quad (4.2)$$

This equation may be expressed as

$$\begin{aligned} f_0(\tau_0, \tau_1, \dots, \tau_n) \\ = e^{-iL_b \tau_0} h_{\text{eq}} \Psi_0(\tau_1, \dots, \tau_n), \end{aligned} \quad (4.3)$$

where we have used Eq. (4.1) and the initial condition Eq. (3.6). Since  $L_b$  commutes with  $h_{\text{eq}}$  it follows that

$$f_0 = h_{\text{eq}} \Psi_0(\tau_1, \dots, \tau_n) = f_0(\tau_1, \dots, \tau_n). \quad (4.4)$$

We now turn to Eq. (2.21). It is easy to show, using Eq. (4.3), that the term  $i\mathcal{L}[f_0]$  is zero. If we now assume spatial uniformity, i.e.,  $\Psi(\vec{R}, \vec{P}; t) \equiv \Psi(\vec{P}, t)$ , the entire right-hand side of Eq. (2.21) is zero. We integrate this expression with respect to  $\tau_0$  and obtain

$$\begin{aligned} i\Psi_1(\tau_0, \tau_1, \dots, \tau_n) - i\Psi_1(0, \tau_1, \dots, \tau_n) \\ = -i\tau_0 \partial \Psi_0 / \partial \tau_1, \end{aligned} \quad (4.5)$$

where we have used the result Eq. (4.1) that  $\Psi_0$  does not vary on the  $\tau_0$  scale. In order to prevent secular behavior we must set

$$\frac{\partial \Psi_0}{\partial \tau_1} = 0. \quad (4.6)$$

It follows that  $\Psi_0$  does not vary on the  $\tau_1$  time scale and

$$\Psi_0 = \Psi_0(\tau_2, \dots, \tau_n). \quad (4.7)$$

Thus we see that the initial variation in  $\Psi_0$  occurs on the "slow" time scale  $\tau_2$ . From Eqs. (4.4) and (4.7) we find

$$f_0 = f_0(\tau_2, \dots, \tau_n). \quad (4.8)$$

Since  $\Psi_1(0, \tau_1, \dots, \tau_n) = 0$  an additional consequence of Eq. (4.6) is that  $\Psi_1 \equiv 0$ , i.e. at all times corrections to  $\Psi_0$  will be  $O(\gamma^2)$ .

We may now integrate Eq. (2.18) with respect to  $\tau_0$  using the result Eq. (4.8). We find

$$\begin{aligned} f_1(\tau_0, \tau_2, \dots, \tau_n) \\ = -i \int_0^{\tau_0} ds e^{-iL_b s} L' h_{\text{eq}} \Psi_0(\tau_2, \dots, \tau_n), \end{aligned} \quad (4.9)$$

where we have used the fact that  $f_1(0, \tau_1, \dots) = 0$ .

With the results  $\Psi_1 \equiv 0$  and Eq. (4.7), Eq. (2.22) may be integrated with respect to  $\tau_0$ . We obtain, after using the assumption of spatial uniformity,

$$i\Psi_2(\tau_0, \tau_1, \dots, \tau_n) - i\Psi_2(0, \tau_1, \dots, \tau_n)$$

$$= -i\tau_0 \left( \frac{\partial \Psi_0}{\partial \tau_2} - \frac{1}{\tau_0} \int_0^{\tau_0} dx \mathfrak{L} [f_1(x, \tau_2, \dots, \tau_n)] \right) \quad (4.10)$$

To prevent secular behavior we must have for asymptotic times on the  $\tau_0$  scale ( $\tau_0 \rightarrow \infty$ ):

$$\frac{\partial \Psi_0}{\partial \tau_2} = - \frac{i}{\tau_0} \int_0^{\tau_0} dx \int_0^x ds \mathfrak{L} [e^{-iL_b s} L' h_{\text{eq}}] \times \Psi_0(\tau_2, \dots, \tau_n), \quad (4.11)$$

where we have substituted Eq. (4.9) for  $f_1$ . The integrand in Eq. (4.11) depends only upon  $s$ ; we may perform the  $x$  integration:

$$\frac{\partial \Psi_0}{\partial \tau_2} = -i \int_0^{\tau_0} ds \left(1 - \frac{s}{\tau_0}\right) \mathfrak{L} [e^{-iL_b s} L' h_{\text{eq}}] \times \Psi_0(\tau_2, \dots, \tau_n). \quad (4.12)$$

We may use the definitions of  $\mathfrak{L}$  and  $L'$  to write

$$\int_0^{\tau_0} ds \{-i\mathfrak{L} [e^{-iL_b s} L' h_{\text{eq}}]\} = \nabla_{\vec{p}} \cdot \int_0^{\tau_0} ds \langle \vec{F}(s) \vec{F} \rangle \cdot [(\vec{P}/mkT) + \nabla_{\vec{p}}]. \quad (4.13)$$

In Eq. (4.13) we have defined the force on the Brownian particle by

$$\vec{F} = -\nabla_{\vec{R}} U, \quad \text{and} \quad \vec{F}(t) = \exp(iL_b t) \vec{F}.$$

The angular bracket denotes an average over the equilibrium distribution  $h_{\text{eq}}$ .

The autocorrelation function of  $\vec{F}$  is computed by determining the equations of motion of the bath particles subject to the condition that the Brownian particle remains fixed. It is reasonable to suppose that this correlation function decays to zero at some finite time on the  $\tau_0$  scale,<sup>13</sup> i.e., its decay is independent of  $\gamma$ . Since Eq. (4.12) is only valid asymptotically on the  $\tau_0$  scale, on taking the limit  $\tau_0 \rightarrow \infty$  one obtains

$$\frac{\partial \Psi_0}{\partial \tau_2} = \zeta \nabla_{\vec{p}} \cdot \left( \frac{\vec{P}}{\gamma^2} + \frac{M}{\beta} \nabla_{\vec{p}} \right) \Psi_0(\tau_2, \dots, \tau_n), \quad (4.14)$$

where we have defined the friction constant

$$\zeta = (\beta/3M) \int_0^{\infty} dt \langle \vec{F}(t) \cdot \vec{F} \rangle, \quad (4.15)$$

and we have made use of the fact that the fluid is isotropic. We also note that the asymptotic condition [and the fact that  $\Psi_2(0, \tau_1, \dots, \tau_n) = 0$ ] requires us to set  $\Psi_2 \equiv 0$  as  $\tau_0 \rightarrow \infty$ . Part of the transient behavior of the Brownian particle distribution function is given by

$$\frac{\partial \Psi_2}{\partial \tau_0} = - \int_{\tau_0}^{\infty} ds \nabla_{\vec{p}} \cdot \langle \vec{F}(s) \vec{F} \rangle \cdot \left( \frac{\vec{P}}{mkT} + \nabla_{\vec{p}} \right) \Psi_0(\tau_2, \dots, \tau_n).$$

Equation (4.14) is correct to order  $\gamma^2$ . It tells us that the important variation of  $\Psi(t)$  first occurs on the "slow"  $\tau_2$  scale. If we now contract our description and return to the proper dimensional variables we obtain for  $\Psi(t)$  the kinetic Fokker-Planck equation

$$\frac{\partial \Psi}{\partial t} = \zeta \nabla_{\vec{p}} \cdot [ \vec{P} + (M/\beta) \nabla_{\vec{p}} ] \Psi(t). \quad (4.16)$$

#### V. THE SPATIALLY INHOMOGENEOUS CASE

Analysis of the case where spatial inhomogeneities exist closely parallels the calculation just presented. The first significant difference occurs when we consider Eq. (2.21); Eqs. (4.1) and (4.3) remain valid. One finds upon integrating Eq. (2.21) with respect to  $\tau_0$

$$i\Psi_1(\tau_0, \tau_1, \dots) = -i\tau_0 \left( \frac{\partial \Psi_0}{\partial \tau_1} + \frac{\vec{P}}{m} \cdot \nabla_{\vec{R}} \Psi_0 \right). \quad (5.1)$$

To prevent secular behavior we must have

$$\Psi_0(\tau_1, \tau_2, \dots, \tau_n) = \exp[-(\vec{P}/m) \cdot \nabla_{\vec{R}} \tau_1] \Psi_0(0, \tau_2, \dots, \tau_n) \quad (5.2)$$

and hence  $\Psi_1 \equiv 0$ . In the case where spatial inhomogeneities exist both  $\Psi_0$  and  $f_0$  vary on the  $\tau_1$  scale; on this time scale the Brownian particle follows a straight line trajectory.

We now turn to Eq. (2.18) and integrate with respect to  $\tau_0$ . After lengthy but straightforward manipulation one finds

$$f_1(\tau_0, \tau_1, \dots, \tau_n) = - \int_0^{\tau_0} ds e^{-iL_b s} h_{\text{eq}} \times [(\vec{P}/m) \cdot \beta \vec{F} + \nabla_{\vec{p}} \cdot \vec{F}] \Psi_0(\tau_1, \dots, \tau_n). \quad (5.3)$$

This result is now substituted into Eq. (2.22) and an integration with respect to  $\tau_0$  performed. We obtain

$$i\Psi_2(\tau_0, \tau_1, \dots, \tau_n) = -i\tau_0 \left\{ \frac{\partial \Psi_0}{\partial \tau_2} - \frac{1}{\tau_0} \int_0^{\tau_0} dx \int_0^x ds \nabla_{\vec{p}} \cdot \langle \vec{F}(s) \vec{F} \rangle \cdot [(\beta \vec{P}/m) + \nabla_{\vec{p}}] \Psi_0(\tau_1, \dots, \tau_n) \right\}. \quad (5.4)$$

An identical argument to that used in the previous section leads to the asymptotic condition  $\Psi_2 \equiv 0$  and

$$\frac{\partial \Psi_0}{\partial \tau_2} = \zeta \nabla_{\vec{p}} \cdot \left( \frac{\vec{P}}{\gamma^2} + \frac{M}{\beta} \nabla_{\vec{p}} \right)$$

$$\times \Psi_0(\tau_1, \tau_2, \dots, \tau_n), \quad (5.5)$$

where we have used the fact that the fluid is isotropic.

We now contract the description taking into account that  $\Psi_0$  varies on both the  $\tau_1$  and  $\tau_2$  time scales,

$$\frac{\partial \Psi}{\partial t} \approx \gamma \frac{\partial \Psi_0}{\partial \tau_1} + \gamma^2 \frac{\partial \Psi_0}{\partial \tau_2} + O(\gamma^3). \quad (5.6)$$

Our final equation becomes, when we return to dimensional variables, exactly the Fokker-Planck Eq. (1.1):

$$\frac{\partial \Psi}{\partial t} = -\frac{\vec{p}}{M} \cdot \nabla_{\vec{R}} \Psi(t) + \zeta \nabla_{\vec{p}} \cdot [\vec{p} + M/\beta \nabla \vec{p}] \Psi(t). \quad (5.7)$$

## VI. CONCLUDING REMARKS

We have presented a derivation, by the multiple-time-scale method, of the Fokker-Planck equation for the Brownian particle distribution function. The method clearly reveals the importance of the existence of widely separated time scales in the problem. Our calculation has explicitly been carried out to order  $\gamma^2$ . In the spatially uniform case our result may be obtained by the projection operator method<sup>2</sup> in conjunction with the double limiting procedure<sup>3</sup>

$$\lambda^2 \rightarrow 0, \quad t \rightarrow \infty; \quad \lambda^2 t = \tau = \text{constant}. \quad (6.1)$$

The double limiting procedure implies the result explicitly displayed by the multiple-time-scale method, i. e. the important variation of  $\Psi$  is on the "slow" time scale  $\tau_2$ . When the system is not spatially uniform, we find that the important variation of  $\Psi$  occurs on the two "slow" time scales  $\tau_1$  and  $\tau_2$ . When this case is considered from the projection-operator point of view, the limiting procedure of Eq. (6.1) will not yield a sensible result. The double limiting procedure can only extract one slow time scale.

It should be emphasized, that the multiple-time-scale method alleges that corrections to Eq. (5.7) will be of order  $\gamma^3$  for all times. There can be no secular terms in the higher order corrections because the method systematically removes this type of behavior.

One of the most intriguing possibilities of the multiple-time-scale method is that it suggests a systematic procedure for obtaining corrections to Eq. (5.7). These "corrections" may be of two types. First, we can inquire about the relaxation from an initial condition that differs from the simple one universally adopted and adopted here. Secondly, we can examine the behavior of  $\Psi$  to orders higher than  $\gamma^2$ . This would involve an analysis of the behavior of  $\Psi_0$  on slower time scales than  $\tau_2$  and a determination of  $\Psi_3, \Psi_4, \dots$ , etc. We are currently considering this question.<sup>14</sup>

The multiple-time-scale method has had considerable success in problems dealing with the kinetic theory of neutral gases and plasmas. In our judgment the method offers attractive possibilities for dealing with a variety of relaxation problems in liquid systems.

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<sup>11</sup>J. E. McCune, G. Sandri, and E. A. Frieman, *Rarified Gas Dynamics* (Academic Press, New York, 1963), Vol. I, Suppl. 2, p. 102.

<sup>12</sup>R. Zwanzig, *J. Chem. Phys.* **40**, 2527 (1964).

<sup>13</sup>It might be well to mention that we are considering the limit of a very large system, i. e. the thermodynamic limit. We do this to avoid all wall effects.

<sup>14</sup>Some results are available for higher orders in  $\gamma$  in Ref. (1).