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## Non-equilibrium fluctuations in a master equation system

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**Abstract.** van Kampen's systematic expansion of the master equation is used to obtain some non-equilibrium properties of a one-dimensional model. We derive the phenomenological equation of motion and to zero order in the expansion parameter  $m/(m+M)$ , we also calculate the velocity autocorrelation function, the fluctuation spectrum and the time-dependent diffusion coefficient for two degrees of departure from equilibrium. We find that the correlation function does not exhibit a long-time tail pattern and finally, for a generalisation of the model considered, we show that for further away from equilibrium situations a memory sets into the system giving rise to a specific structure of the hydrodynamical equation for the local concentration variable.

### 1. Introduction

The problem of determining the influence of fluctuations around the macroscopic behaviour of a many-body system has received much attention in recent years and has given rise to much literature. This influence has been studied in a large variety of phenomena such as fluctuations in the Boltzmann equation, fluctuating hydrodynamics or phenomena of the type of phase transitions where the system is in an unstable situation.

The most widely used theoretical tools in the study of time-varying fluctuations have long been the phenomenological Fokker–Planck equation and the Langevin equation (Zwanzig 1972, Zwanzig *et al* 1972, Kawasaki 1973, 1974), although they have been subjected to serious objections (van Kampen 1976, García-Colín 1979). Methods based on extensions of the microscopic Mori approach, that form the basis of mode-mode coupling theory, have also been used (García-Colin 1979, Keyes and Oppenheim 1973, Kapral *et al* 1973, 1974).

Another type of mesoscopic approach is based on the master equation governing the probability distribution of the variables involved. It applies to non-stationary states far from equilibrium as well as to stationary states. The main problem is to solve this equation, or, in the case of nonlinear systems, to find a suitable approximation method. van Kampen (1961, 1965) has introduced a systematic expansion procedure based on the reciprocal size of the system. The purpose of this paper is to use this systematic expansion of the master equation to calculate the non-equilibrium fluctuations and their effect on some properties of a well known model, the so-called Rayleigh piston (Rayleigh 1902, Alkemade *et al* 1963, Hoare 1971). In this model a massive Brownian particle of mass  $M$  is constrained to move in one dimension and is subject to impulsive

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collisions with the light molecules of mass  $m$  of a Knudsen gas in equilibrium. This model is itself simple enough for easy, explicit mathematical description, yet real enough to embody some basic features of fluctuation phenomena.

We have considered this model in a previous paper (Rodríguez and García-Colín 1978, to be referred to as I) where we calculated the equilibrium fluctuations and the diffusion coefficient up to second order in the small parameter  $m/(m+M)$ . Here we consider the non-equilibrium situation and from the master equation we derive the macroscopic or phenomenological equation when the system is near and further away from equilibrium. The degree of departure from equilibrium is measured in powers of a function  $\phi(t)$  which is introduced into the expansion procedure. We then obtain the velocity-velocity correlation function to order zero in the small parameter mentioned above for two degrees of departure from equilibrium. In terms of this correlation we also obtain the fluctuations spectrum and the diffusion coefficient for the massive particle.

The organisation of the paper is as follows. In § 2 we summarise the main ideas behind the systematic expansion as used for this model. In § 3 we derive the macroscopic equation of motion and explicitly point out its main features especially for away from equilibrium situations. The fluctuations in the system are studied in § 4. The calculations lead to an explicit expression for the velocity-velocity correlation function which corresponds to a stationary process when, to order zero in the expansion parameter, one considers situations close to and further away from equilibrium. The fluctuation spectrum and the time-dependent diffusion coefficient are computed in §§ 5 and 6, respectively. The main results are that not close to equilibrium the former one is no longer a single Lorentzian and that the diffusion coefficient is no longer a simple function of temperature and density. Also it does not exhibit a long-time tail pattern as one could have expected from similar situations. It is also shown that further away from equilibrium the diffusion coefficient depends explicitly on the initial conditions, that is, it displays a memory. The consequences of this result are investigated in § 7 where we generalise the model by assuming that there may be several heavy particles immersed in the gas, so that a local concentration variable can be defined, and we deduce the form of the hydrodynamical equation of motion for this variable. The final § 8 summarises the main results of this work and contains some further physical remarks.

## 2. The systematic expansion

The velocity  $V$  of a heavy particle is the stochastic variable of our problem and we consider it to be a continuous Markovian process. From considerations of momentum and energy conservation it can be shown that the corresponding transition probability per unit time is given by

$$W(V'|V) = \frac{\nu}{4} \left( \frac{m+M}{m} \right)^2 |V - V'| f \left( \frac{m+M}{2m} V' - \frac{M-m}{2m} V \right) \quad (1)$$

(see van Kampen 1961, equation (32)) where  $\nu$  is the linear density of gas molecules and  $f$  stands for its velocity distribution. Therefore, the velocity probability distribution  $P(V, t)$  for the Rayleigh particle obeys the continuous master equation

$$\frac{\partial}{\partial t} P(V, t) = \int_{-\infty}^{\infty} \{W(V|V')P(V', t) - W(V'|V)P(V, t)\} dV'. \quad (2)$$

Following van Kampen's general method we shall perform a systematic expansion of this equation in powers of a small parameter  $\Omega$ . The first step consists in specifying  $\Omega$  and the dependence of the transition probability  $W$  on it. We choose as our expansion parameter the ratio

$$\Omega = (m + M)/m \tag{3}$$

and we introduce the variable

$$y = (m + M)V/m. \tag{4}$$

In terms of it the transition  $W$  is given by

$$W(y, \Delta y) = \frac{1}{4\nu} |\Delta y| f(V + \frac{1}{2}\Delta y) \tag{5}$$

where  $\Delta y$  measures the size of the jump in the stochastic variable  $y$ . Note that this form of  $W$  is entirely independent of  $\Omega$  in agreement with van Kampen's procedure.

Now we have to postulate the way in which  $P(V, t)$  depends on  $\Omega$ . In van Kampen's method it is proposed that  $P(V, t)$  has a sharp peak located at some point  $\Omega\psi(t)$  with a width of order  $\Omega^{1/2}$ . This assumption is expressed formally by transforming the stochastic variable  $y$  to a new variable  $x$  defined by

$$y = \Omega\psi(t) + \Omega^{1/2}x \quad \text{or} \quad V = \psi(t) + \Omega^{-1/2}x \tag{6}$$

where  $\psi(t)$  is some time-dependent function which has to be determined. This is a crucial assumption that explicitly contains a central-limit theorem argument. Its correctness has to be justified *a posteriori* by showing that it is actually possible to choose  $\psi(t)$  in such a way that  $x$  turns out to be of order unity. Therefore, as a consequence of (6)  $P(V, t)$  transforms into the probability density distribution  $\pi(x, t)$ . Starting from (2) and using (6) it is only a matter of algebra to obtain a transformed equation for  $\pi(x, t)$  which may be systematically expanded in powers of  $\Omega^{-1/2}$ . The explicit steps of this transformation and the resulting equations may be found in van Kampen (1965, 1976).

### 3. The macroscopic equation

The jump or derivative moments of the probability distribution  $W$  are defined by

$$\alpha_n(V) = \int_{-\infty}^{\infty} (\Delta y)^n W(V, \Delta y) d\Delta y. \tag{7}$$

Using the transformation defined in equation (6) they can be expanded in powers of  $\Omega^{-1/2}$ , that is,

$$\alpha_n(\psi(t) + \Omega^{-1/2}x) = \sum_{m=0}^{\infty} \frac{1}{m!} \Omega^{-m/2} \alpha_n^{(m)}(\psi(t)) x^m = \alpha_{n,0}(\psi) + \Omega^{-1/2} \alpha_{n,1} + \dots \tag{8}$$

Here  $\alpha_n^{(m)}$  denotes the  $m$ th derivative of  $\alpha_n$  with respect to its argument and evaluated at  $x = 0$ . Note that since in equilibrium  $\psi(t = \infty) = 0$  the jump moments are constants, but for non-equilibrium states they will be functions of  $\psi$ .

The expansion mentioned in the previous section yields the following results (van Kampen 1979): The leading terms are of order  $\Omega^{1/2}$  and they can be made to cancel if

$\psi(t)$  satisfies the equation

$$\frac{d}{dt^*} \psi(t) = \alpha_{1,0}(\psi(t)) \quad (9)$$

where  $t^* = \Omega^{-1}t$ . There are no fluctuations in this equation since it is obtained in the limit when  $\Omega \rightarrow \infty$ . Moreover, it is a deterministic equation and, therefore, it can be identified with the macroscopic equation for the system. For the present model we can explicitly calculate  $\alpha_{1,0}(\psi)$  and obtain the macroscopic or phenomenological equation for the system. Furthermore, since in equilibrium  $\psi(t = \infty) = 0$ , an expansion of  $\alpha_{1,0}$  in powers of  $\psi$  will describe the macroscopic behaviour of the system as it moves away from equilibrium. In the appendix it is shown that to order  $\Omega^0$

$$\alpha_{1,0}(\psi) = -\frac{8\nu}{(2\pi)^{1/2}} \left(\frac{k_B T}{m}\right)^{1/2} \left(\psi + \frac{1}{6} \frac{m}{k_B T} \psi^3\right) + O(\psi^5). \quad (10)$$

For the purpose of the calculation of fluctuations we shall need the second derivative moment of  $W$ . In the appendix it is also shown that

$$\alpha_{2,0}(\psi) = \frac{16\nu}{(2\pi)^{1/2}} \left(\frac{k_B T}{m}\right)^{1/2} \left(1 + \frac{3}{\sqrt{2}} \frac{m}{k_B T} \psi^2\right) + O(\psi^4). \quad (11)$$

Note that if we set  $\psi = 0$  in these equations we recover the corresponding equilibrium values obtained previously in I, namely

$$\alpha_1^{eq} = 0 \quad \alpha_2^{eq} = \frac{16\nu}{(2\pi)^{1/2}} \left(\frac{k_B T}{m}\right)^{1/2}. \quad (12)$$

Then, according to (9) and (10), and up to third order in  $\psi$ , the resulting expansion for the macroscopic equation is given by

$$\frac{d}{dt^*} \psi = -8\nu \left(\frac{k_B T}{2\pi m}\right)^{1/2} \left(\psi + \frac{1}{6} \frac{m}{k_B T} \psi^3\right) + O(\psi^5). \quad (13)$$

It therefore follows that the linearised equation can be written as

$$d\psi(t)/dt = -\gamma\psi(t) \quad (14)$$

where for the damping coefficient  $\gamma$  we obtain

$$\gamma = \frac{4\nu}{m + M} \left(\frac{2mk_B T}{\pi}\right)^{1/2} \quad (15)$$

and the linearised solution, for given  $\psi_0 \equiv \psi(t = 0)$ , is

$$\psi(t) = \psi_0 e^{-\gamma t} + O(\psi^3). \quad (16)$$

Equation (14) corresponds to the familiar damping law for the velocity of the Rayleigh particle (Hoare 1971),  $\dot{V} = -\gamma V$ . This macroscopic equation has one stationary solution and all the other solutions converge to it. Therefore all solutions are asymptotically stable, and the effect of an instantaneous fluctuation dies out so that a continually acting perturbation has no cumulative effect. In the stationary state the effect of the fluctuations is balanced by the macroscopic tendency of returning to the stationary solution, thus satisfying the fluctuation-dissipation theorem.

The next order approximation to the macroscopic equation is given by

$$d\psi/dt = -\gamma\psi - \gamma_1\psi^3 + O(\psi^5) \tag{17}$$

with

$$\gamma_1 = \frac{4\nu}{3} \frac{m}{m+M} \left( \frac{m}{2\pi k_B T} \right)^{1/2}. \tag{18}$$

From it we get the first nonlinear correction

$$\psi(t) = \psi_0 e^{-\gamma t} [1 + \Gamma\psi_0^2(1 - e^{-2\gamma t})]^{-1/2} \tag{19}$$

for given  $\psi_0$ , with

$$\Gamma \equiv \gamma_1/\gamma = \frac{1}{6}m/k_B T. \tag{20}$$

#### 4. The fluctuations

To order  $\Omega^0$  in the systematic expansion of the master equation we have that (van Kampen 1979)

$$\frac{\partial}{\partial t} \pi(x, t) = -\alpha'_{1,0}(\psi) \frac{\partial}{\partial x} x\pi + \frac{1}{2}\alpha_{2,0}(\psi) \frac{\partial^2}{\partial x^2} \pi. \tag{21}$$

This is a Fokker-Planck equation with time-dependent coefficients from which we may derive equations for the first moments of  $\pi$ . Thus we obtain that

$$d\langle x \rangle/dt = \alpha'_{1,0}(\psi)\langle x \rangle \tag{22}$$

$$d\langle x^2 \rangle/dt = 2\alpha'_{1,0}(\psi)\langle x^2 \rangle + \alpha_{2,0}(\psi). \tag{23}$$

Note that the first equation is identical to the variational equation associated with equation (9), that is, the equation for the difference between two neighbouring solutions. Since from (10) we know that  $\alpha'_{1,0} < 0$ , we conclude that macroscopic stability determines that the average  $\langle x \rangle$  of the fluctuations will not grow with time and therefore the fluctuations will remain small at all times.

The equations for the average and the variance can be solved exactly for given  $x_0 = \langle x(\psi_0) \rangle$ ,  $x_0^2 = \langle x^2(\psi_0) \rangle$ . We find that

$$\langle x(\psi) \rangle = \frac{x_0}{\alpha_{1,0}(\psi_0)} \alpha_{1,0}(\psi) \tag{24}$$

and

$$\langle x^2(\psi) \rangle = [\alpha_{1,0}(\psi)]^2 \left( \int [\alpha_{1,0}(\psi)]^{-3} \alpha_{2,0}(\psi) d\psi + x_0^2 - \psi_0 \frac{\alpha_{2,0}(\psi_0)}{\alpha_{1,0}(\psi_0)} \right). \tag{25}$$

In order to calculate the fluctuation spectrum, first we have to compute the autocorrelation function defined as the limit of

$$\langle x(t_1)x(t_2) \rangle - \langle x(t_1) \rangle \langle x(t_2) \rangle \tag{26}$$

when  $t_1 \rightarrow \infty$ ,  $t_2 \rightarrow \infty$ , with fixed  $t_2 - t_1$ . To this end we calculate  $\langle x(t_1)x(t_2) \rangle$  starting from the well known equality

$$\pi(x_1 t_1; x_2 t_2) = \pi(x_1 t_1) \pi(x_2 t_2 | x_1 t_1) \quad t_2 > t_1 \tag{27}$$

from which it follows that

$$\langle x_1(t_1)x_2(t_2) \rangle = \int dx_1 x_1(t_1) \pi(x_1 t_1) \langle x(t_2 - t_1) \rangle_{x_1}. \quad (28)$$

If we use equations (24) and (25) in equation (28), we find that

$$\begin{aligned} \langle x_1(t_1)x_2(t_2) \rangle &= \frac{1}{\alpha_{1,0}(\psi_0)} \alpha_{1,0}[\psi(t_2 - t_1)] [\alpha_{1,0}(\psi(t_1))]^2 \\ &\times \left( \int [\alpha_{1,0}(\psi(t_1))]^{-3} \alpha_{2,0}(\psi(t_1)) d\psi + x_0^2 - \psi_0 \frac{\alpha_{2,0}(\psi_0)}{\alpha_{1,0}(\psi_0)} \right). \end{aligned} \quad (29)$$

Note that this is an exact result which, in principle, could be evaluated using the exact expressions for  $\psi$  and the jump moments involved. However, since we have only calculated the macroscopic equations near equilibrium, we shall evaluate equation (29) using for the jump moments the first terms containing  $\psi$  in equations (10) and (11), namely

$$\alpha_{1,0}(\psi) = -8\nu (k_B T / 2\pi m)^{1/2} \psi \quad (30)$$

$$\alpha_{2,0}(\psi) = 16\nu \left( \frac{k_B T}{2\pi m} \right)^{3/2} \left( 1 + \frac{3}{\sqrt{2}} \frac{m}{k_B T} \psi^2 \right). \quad (31)$$

Accordingly we obtain that

$$\langle x(t_1)x(t_2) \rangle = \frac{k_B T}{m} \frac{1}{\psi_0} \psi(t_2 - t_1) (1 + A\psi^2(t_1) + B\psi^2(t_1) \log \psi(t_1)) \quad (32)$$

with

$$A = \frac{32}{\pi} \nu^2 \psi_0^2 \left[ x_0^2 + 2 \frac{k_B T}{m} \left( 1 + \frac{3}{\sqrt{2}} \frac{m}{k_B T} \psi_0^2 \right) \right] \quad B = -\frac{6}{\sqrt{2}} \frac{m}{k_B T}.$$

In a similar fashion we find the average  $\langle x(t) \rangle$  as an implicit function of  $t$ . From equations (24) and (30) we have that

$$\langle x(t) \rangle = x_0 \psi(t). \quad (33)$$

Now we can calculate the velocity-velocity correlation function. If we first insert equation (19) into equations (32) and (33), and if the resulting expressions are substituted into equation (26), after taking the indicated limits we find that

$$\langle x(0)x(\tilde{t}) \rangle = (k_B T / m) e^{-\gamma \tilde{t}} [1 + \Gamma \psi_0^2 (1 - e^{-2\gamma \tilde{t}})]^{-1/2} \quad (34)$$

with  $\tilde{t} = t_2 - t_1$ . This correlation corresponds to a stationary process and near equilibrium ( $\Gamma \rightarrow 0$ ) it reduces to the usual exponential decay.

## 5. The fluctuation spectrum

The connection between the fluctuations spectrum and the autocorrelation function for a stationary process with a finite correlation time is given by the Wiener-Khintchine

theorem

$$S(w) = \frac{2}{\pi} \int_0^\infty \langle x(0)x(t) \rangle \cos wt \, dt. \tag{35}$$

If we introduce into this expression the correlation function given by equation (34) we find that the first nonlinear correction to the spectrum is given by

$$S(w) = \frac{2}{\pi} \frac{k_B T}{m} \left( \left(1 - \frac{1}{2}\Gamma\psi_0^2\right) \frac{\gamma}{\gamma^2 + w^2} + \frac{1}{2}\Gamma\psi_0^2 \frac{3\gamma}{9\gamma^2 + w^2} \right) \tag{36}$$

which is a combination of Lorentzians<sup>†</sup>. Clearly, near equilibrium ( $\Gamma \rightarrow 0$ ) it reduces to

$$S(w) = \frac{2}{\pi} \frac{k_B T}{m} \frac{\gamma}{\gamma^2 + w^2}. \tag{37}$$

If we use equation (15) this spectrum can be expressed as an explicit function of  $T$ , i.e.

$$S(w) = \Lambda T^{3/2} (\lambda T + w^2)^{-1} \tag{38}$$

with

$$\Lambda = \frac{8\sqrt{2}}{\pi^{3/2}} \nu \frac{m}{m+M} \left(\frac{k_B}{m}\right)^{3/2} \tag{39}$$

and

$$\lambda = \frac{32\nu^2}{\pi} \frac{mk_B}{(m+M)^2}. \tag{40}$$

### 6. The diffusion coefficient

Another quantity of interest that we can compute from the autocorrelation function is the time-dependent diffusion coefficient defined by (Dorfman 1975)

$$D^{(0)}(t) = \int_0^t dt' \langle x(0)x(t') \rangle. \tag{41}$$

Using equation (34) we find that in the moderately nonlinear regime

$$D^{(0)}(t) = \frac{k_B T}{m} \frac{1}{\gamma} \left[ 1 - \frac{1}{3}\Gamma\psi_0^2 - \left(1 - \frac{1}{2}\Gamma\psi_0^2\right) e^{-\gamma t} - \frac{1}{6}\Gamma\psi_0^2 e^{-3\gamma t} \right] \tag{42}$$

and for the near equilibrium limit ( $\Gamma \rightarrow 0$ ) it reduces to

$$D^{(0)}(t) = \frac{k_B T}{m} \frac{1}{\gamma} (1 - e^{-\gamma t}). \tag{43}$$

If we use equation (15) in the last equation, the diffusion coefficient can be written as an explicit function of the temperature and the density, i.e.

$$D^{(0)}(t) = \frac{1}{4} \left(\frac{\pi}{2}\right)^{1/2} \frac{1}{\nu} \frac{m+M}{m} \left(\frac{k_B T}{m}\right)^{1/2} \left\{ 1 - \exp\left[-\frac{4\nu}{m+M} \left(\frac{2mk_B T}{\pi}\right)^{1/2} t\right] \right\}. \tag{44}$$

<sup>†</sup> This result agrees with those obtained by Hoare (1971), Hoare and Rahman (1974) using a different approach.



Therefore, near equilibrium the diffusion coefficient varies as  $T^{1/2}$  and depends upon the density  $\nu$  varying inversely with it. As could be expected, this dependence on  $T$  and  $\nu$  is the same as the one obtained from the first approximation to the Chapman–Enskog expression for the diffusion coefficient (Chapman and Cowling 1970). On the other hand, as the system moves further away from equilibrium the diffusion coefficient, given by equation (42), is no longer a simple function of temperature and density, since  $\Gamma$  is also a function of  $T$  as given by equation (20).

## 7. Generalisation

From the results of the previous section we observe that the near equilibrium expression for the time-dependent diffusion coefficient, given by equation (43), does not depend on the initial value  $\psi_0$ , as expected. On the other hand, further away from equilibrium it depends explicitly on the initial condition  $\psi_0$ , as shown in equation (43). Therefore we may conclude that as the departure from equilibrium increases a memory appears in the system. In order to investigate this idea in more detail, we generalise our model by assuming that we have several massive particles instead of one so that we can define a local concentration variable  $\langle C(\mathbf{r}, t) \rangle$ ; here the angular brackets indicate a non-equilibrium average. As a first approximation we consider that all the heavy particles are independent. The fact that the total mass of the heavy particles is conserved is expressed by the continuity equation

$$\frac{\partial}{\partial t} \langle C(\mathbf{r}, t) \rangle + \nabla \cdot \langle \mathbf{j}^c(\mathbf{r}, t) \rangle = 0 \quad (45)$$

where  $\langle \mathbf{j}^c(\mathbf{r}, t) \rangle$  is the concentration current.

If we assume that all the properties of the system vary slowly in space and time, i.e. for small frequencies, then it is well known that the local concentration obeys the constitutive relation

$$\langle \mathbf{j}^c(\mathbf{r}, t) \rangle = -D \nabla \langle C(\mathbf{r}, t) \rangle \quad (46)$$

where  $D$  is a positive constant. With this assumption and the conservation law (45) we can then obtain the familiar diffusion equation for  $\langle C(\mathbf{r}, t) \rangle$ , i.e.

$$\frac{\partial}{\partial t} \langle C(\mathbf{r}, t) \rangle - D \nabla^2 \langle C(\mathbf{r}, t) \rangle = 0. \quad (47)$$

For an infinitely extended system and for given initial conditions this equation is trivially solved by performing a Fourier transformation in space

$$\langle C(\mathbf{k}, t) \rangle = \int d\mathbf{r} \exp(-i\mathbf{k} \cdot \mathbf{r}) \langle C(\mathbf{r}, t) \rangle \quad (48)$$

and a Laplace transformation in time

$$\langle C(\mathbf{k}, z) \rangle = \int_0^\infty dt e^{izt} \langle C(\mathbf{k}, t) \rangle \quad \text{Im } z > 0 \quad (49)$$

where  $\mathbf{k}$  is the wavevector and  $z$  the complex frequency of the fluctuation. Then from

(47) we explicitly obtain

$$\langle C(\mathbf{k}, z) \rangle = \frac{i}{z + iDk^2} \langle C(\mathbf{k}, t = 0) \rangle. \tag{50}$$

Let us now consider larger frequencies. In this case  $C(\mathbf{r}, t)$  varies more rapidly and we should therefore expect a time lag between  $C$  and  $f^c$ . Hence, instead of equation (46) we could try a more general constitutive relation such as

$$\langle j^c(\mathbf{r}, t) \rangle = - \int_0^t D(t-t') \nabla \langle C(\mathbf{r}, t') \rangle dt'. \tag{51}$$

Here the function  $D(t-t')$ , a time-dependent diffusion coefficient, is called a memory function and it incorporates in a causal way the effect of all the fast processes occurring in the system. Note that since we have found the explicit expressions for  $D(t-t')$  we can evaluate the current  $j^c(\mathbf{r}, t)$  and from it the continuity equation (45). In this way we can then obtain a hydrodynamical equation for  $\langle C(\mathbf{r}, t) \rangle$  which would be the analogue of equation (47). In order to do this we observe that the expressions found for the time-dependent diffusion coefficient, as given by equations (42) and (43), depend on time in an exponential form, i.e.

$$D(t-t') = (d/\tau) \exp[-(t-t')/\tau]. \tag{52}$$

Here the relaxation time  $\tau$  associated with the rapid processes and the coefficient  $d$  could be identified directly from equation (42); however their explicit form is not needed since the essential point of our discussion is to find the structure of the corresponding solution for  $\langle C(\mathbf{r}, t) \rangle$ . Therefore, inserting this equation into equation (51), putting all into the conservation law (45) and performing the Fourier-Laplace transformation mentioned above, we find that

$$\langle C(\mathbf{k}, z) \rangle = \frac{i}{z + ik^2 d/(1 - iz\tau)} \langle C(\mathbf{k}, t = 0) \rangle. \tag{53}$$

From this expression we can obtain the response function (see Forster 1975, ch 2 and 3)

$$\chi(k, z) = \frac{ik^2 d/(1 - iz\tau)}{z + ik^2 d/(1 - iz\tau)} \chi \tag{54}$$

and its absorptive part

$$\chi''(k, \omega) = \frac{\omega k^2 d}{\omega^2 + d^2(k^2 - \omega^2 \tau/d)^2} \chi. \tag{55}$$

If we now transform back to the variables  $\mathbf{r}$  and  $t$ , we conclude that equations (53)–(55) are equivalent to the following hydrodynamical equation of motion for  $\langle C(\mathbf{r}, t) \rangle$

$$\left[ \frac{\partial^2}{\partial t^2} + \frac{1}{\tau} \left( \frac{\partial}{\partial t} - d \nabla^2 \right) \right] \langle C(\mathbf{r}, t) \rangle = 0. \tag{56}$$

### 8. Discussion

In this last section we should like to summarise briefly the main results obtained throughout this paper. Starting from the master equation and using the systematic

expansion introduced by van Kampen, we have obtained the phenomenological equation for the average velocity of the Rayleigh particle near and slightly further away from equilibrium. The degree of departure from equilibrium is measured in powers of the function  $\psi(t)$ , as discussed in § 2. It is important to emphasise that in our discussion the size of the system, as measured by the parameter  $\Omega$ , has always been kept constant. It would be of interest to investigate the effects of driving the system away from equilibrium and at the same time varying its size.

Next, to order zero in  $\Omega$  we have calculated the non-equilibrium fluctuations and their influence on the time-dependent diffusion coefficient. We found that no long-time tail pattern emerges to the orders considered. Furthermore, not close to equilibrium the diffusion coefficient exhibits an explicit dependence on the initial conditions, indicating the appearance of a memory in the system; the form of the memory kernel does not have to be postulated, but emerges naturally from the calculations. In order to examine the implications of this fact we generalised the model by allowing for the possibility of having several independent massive particles, so that a local concentration of them can be defined. Then we deduced the response function and the form of the hydrodynamical equation for the local concentration variable.

It may also be remarked that this model can be generalised to three dimensions but we expect that, in spite of the isotropy of the system, effects such as the persistence of the velocity would have to be taken into account explicitly.

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### Appendix

We calculate explicitly the derivative moments  $\alpha_{1,0}(\psi)$  and  $\alpha_{2,0}(\psi)$ . According to definition (7) and using (5) we have that

$$\alpha_1(V) = \frac{v}{4} \left( \frac{m}{2\pi k_B T} \right)^{1/2} \exp\left( -\frac{m}{2k_B T} V^2 \right) I \quad (\text{A1})$$

where

$$I = \int_{-\infty}^{\infty} \Delta y |\Delta y| \exp\left( -\frac{m}{2k_B T} \left( \frac{1}{4} \Delta y^2 + V \Delta y \right) \right) d\Delta y. \quad (\text{A2})$$

If we define

$$\mu = \frac{m}{8k_B T} \quad \eta = \frac{m}{2k_B T} V \quad (\text{A3})$$

and if

$$u = -\Delta y \quad (\text{A4})$$

the integral  $I$  can be written as

$$I = -2 \int_0^\infty u^2 e^{-\mu u^2} \sinh \eta u \, du. \tag{A5}$$

Evaluating this integral (Gradshteyn and Ryzhik 1965, p 365) and using (73) we obtain that

$$\alpha_1(V) = -2\nu \frac{k_B T}{m} \left(1 + \frac{m}{k_B T} V^2\right) \Phi \left[ V \left(\frac{m}{2k_B T}\right)^{1/2} \right] - 4\nu V \left(\frac{k_B T}{m}\right)^{1/2} \exp\left(-\frac{m}{2k_B T} V^2\right) \tag{A6}$$

where  $\Phi$  stands for the error function. Using for  $V$  the transformation defined by equation (6) and the expansion (8) we obtain equation (10).

Similarly, from definition (7) and using the distribution function (5) we can express the second derivative moment as

$$\alpha_2(V) = \frac{\nu}{4} \left(\frac{m}{2\pi k_B T}\right)^{1/2} \exp\left(-\frac{m}{2k_B T} V^2\right) J \tag{A7}$$

where

$$J = \int_{-\infty}^\infty (\Delta y)^2 |\Delta y| \exp\left(-\frac{m}{2k_B T} (\frac{1}{4}\Delta y^2 + V\Delta y)\right) d\Delta y. \tag{A8}$$

If we use (A3) and (A4),  $J$  may be expressed in the form

$$J = 2 \int_0^\infty u^3 e^{-\mu u^2} \cosh \eta u \, du. \tag{A9}$$

The value of this integral is given by (Gradshteyn and Ryzhik 1965, p 366)

$$J = \Gamma(4)(2\mu)^{-2} \exp(\eta^2/8\mu) (D_{-4}(z) + D_{-4}(-z)) \tag{A10}$$

where  $z = \eta/\sqrt{2\mu}$  and  $D_{-4}(z)$  represents the parabolic cylinder function defined by (Gradshteyn and Ryzhik 1965, p 1064)

$$D_{-4}(z) = \frac{1}{8}(2+z^2) e^{-z^2/4} - \frac{1}{8}\sqrt{\pi/2} z(3+z^2) e^{z^2/4} (1 - \Phi(z/\sqrt{2})). \tag{A11}$$

On substituting in (A10) we obtain

$$J = 32 \left(\frac{k_B T}{m}\right)^2 [2 + z^2 + \sqrt{\pi/2} z(3+z^2) e^{z^2/2} \Phi(z)] \tag{A12}$$

and from (A7) we finally obtain

$$\alpha_2(V) = \frac{8\nu}{\sqrt{2\pi}} \left(\frac{k_B T}{m}\right)^{3/2} \left[ \left(2 + \frac{m}{k_B T} V^2\right) \exp\left(-\frac{m}{2k_B T} V^2\right) + \left(\frac{m\pi}{2k_B T}\right)^{1/2} \left(3 + \frac{m}{k_B T} V^2\right) V \Phi(V\sqrt{m/k_B T}) \right]. \tag{A13}$$

If we now transform  $V$  according to (6), then the first term in the expansion (8) is given by (11).

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