

## LETTER TO THE EDITOR

# Energy and particle number self-diffusion of a classical particle in the potential of randomly fixed scatterers

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**Abstract.** Low  $k, \omega$  fluctuation spectra of the densities of the above two conserved quantities are evaluated using canonical ensemble averages. The effect of other conserved densities is determined for hard sphere potentials where the diffusivities can be expressed in terms of the self-diffusion constant.

The dynamics of a classical particle moving in the potential of randomly fixed scatterers has received increasing attention recently (Bruin 1978, Lewis and Tjon 1978, Alder 1978, Alder and Alley 1978, Alley and Alder 1979, Keyes and Mercer 1979, Götze *et al* 1981: for a survey up to 1974 see Hauge 1974). Such a system represents a model for the motion of a tagged particle in the dynamical environment of, e.g., a fluid and besides that the classical analogue for the problem of electron localisation by disorder (Thouless 1979). Furthermore, various modifications (van Beijeren 1980) have been studied to investigate mathematical problems (Spohn 1980) related to the foundation of statistical mechanics. Here I want to elucidate the low  $k, \omega$  fluctuation dynamics of the densities of the conserved quantities of the above system.

A particular realisation might be obtained from a fluid in thermal equilibrium at temperature  $T$  with a particle  $(\mathbf{r}_0(t), \mathbf{p}_0(t))$  immersed in it by freezing in all positions  $\{\mathbf{r}_n; n = 1 \dots N_s\}$  of the bath of scatterers. Then the average of a dynamical quantity  $A(\mathbf{r}_0, \mathbf{p}_0; \{\mathbf{r}_n\})$  is naturally an ensemble average over the phase space variables of the system at the time of the quench:

$$\langle A \rangle = \frac{\int d\mathbf{p}_0 d\mathbf{r}_0 d\{\mathbf{r}_n\} A \exp[-\beta(H_0 + U)]}{\int d\mathbf{p}_0 d\mathbf{r}_0 d\{\mathbf{r}_n\} \exp[-\beta(H_0 + U)]}. \quad (1)$$

Here  $U$  is the potential energy of the bath particles and

$$H_0 = (p_0^2/2m) + \sum_{n=1}^{N_s} u_0(|\mathbf{r}_0 - \mathbf{r}_n|) \quad (2)$$

is the energy of the moving particle. The variance of the momentum distribution is determined by the temperature of the  $d$ -dimensional bath before the quench

$$\beta^{-1} = k_B T = \frac{1}{d} \frac{\langle p_0^2 \rangle}{m}. \quad (3)$$

Statistical weights other than  $\exp(-\beta U)$  for the scatterer configurations and  $\exp(-\beta H_0)$  for the initial values are conceivable but lead further away from the original physical system.

The energy of the moving particle is a constant of the motion since collisions with fixed scatterers are elastic. However, the value of  $H_0$  fluctuates as a consequence of different initial conditions in different scatterer environments, unless these fluctuations are suppressed by choosing (Hauge 1974, Bruin 1978, Lewis and Tjon 1978, Alder 1978, Alder and Alley 1978, Alley and Alder 1979, Keyes and Mercer 1979, Götze *et al* 1981, Lagar'kov and Sarychev 1975, Lagar'kov and Sergeev 1978) a microcanonical ensemble  $\delta(H_0 - E_0)$ . Such a restriction eliminates those interesting dynamical effects which are investigated here. Since the momentum  $p_0(t)$  is not conserved, one concludes that fluctuations of the densities

$$\begin{aligned} a_1(\mathbf{k}, t) &= \rho(\mathbf{k}, t) \\ &= \exp[-i\mathbf{k} \cdot \mathbf{r}_0(t)] \\ a_2(\mathbf{k}, t) &= \varepsilon(\mathbf{k}, t) - \frac{\langle \varepsilon(-\mathbf{k})\rho(\mathbf{k}) \rangle}{\langle \rho(-\mathbf{k})\rho(\mathbf{k}) \rangle} \rho(\mathbf{k}, t) \\ &= \delta H_0 \exp[-i\mathbf{k} \cdot \mathbf{r}_0(t)] \end{aligned} \quad (4)$$

of the two conserved quantities  $N_0 = 1$  and  $\delta H_0 = H_0 - \langle H_0 \rangle$  relax diffusively towards their mean values in the limit of small  $k, \omega$ . Hence in that limit one expects the spectra  $S_{\nu\mu}(k, \omega)$  of the correlation functions of the above densities to be given by the matrix

$$S(k, \omega) = -\text{Im}[\omega + ik^2 D]^{-1} S(k, t = 0). \quad (5)$$

The equal-time structure function matrix is, by the definition (Schofield 1966) of  $a_2(\mathbf{k}, t)$ , diagonal:

$$\begin{aligned} S_{\nu\mu}(k, t = 0) &= \langle \delta a_\nu^*(k) \delta a_\mu(\mathbf{k}) \rangle \\ &= \begin{pmatrix} 1 & 0 \\ 0 & \langle (\delta H_0)^2 \rangle \end{pmatrix} \end{aligned} \quad (6)$$

and furthermore independent of  $k$ . Using the continuity equations

$$\partial_t a_\nu(\mathbf{k}, t) = -i\mathbf{k} \cdot \mathbf{v}_0(t) a_\nu(\mathbf{k}, t)$$

one can express the positive semidefinite matrix  $D_{\nu\mu}$  of diffusivities via Kubo relations in terms of Green-Kubo integrals:

$$\begin{aligned} DS(t = 0) &= \lim_{\omega \rightarrow 0} \lim_{k \rightarrow 0} \frac{\omega^2}{k^2} S(k, \omega) \\ &= \frac{1}{d} \int_0^\infty dt \left\langle \mathbf{v}_0(t) \cdot \mathbf{v}_0 \begin{pmatrix} 1 & \delta H_0 \\ \delta H_0 & (\delta H_0)^2 \end{pmatrix} \right\rangle \end{aligned} \quad (7)$$

which are assumed to be nonzero. Vanishing diffusivities require special treatment (Lücke 1981).

Since the particle's velocity  $\mathbf{v}_0(t)$  in the potential landscape of the scatterers depends on the energy  $H_0$ , the time dependence of the above correlation functions is quite different and does not necessarily lead to simple relations between the diffusivities (Lücke 1981). In particular, the off-diagonal diffusivities are nonzero. This reflects the statistical

coupling between fluctuations of number density and energy density caused by the statistical factor  $\delta H_0$  in equation (4). Consequently the fluctuation spectra (5) of the auto-correlation functions

$$S_{vv}(k, \omega) = -\text{Im}[\omega + ik^2 D_{vv} + k^4 D_{12} D_{21} / (\omega + ik^2 D_{\mu\mu})]^{-1} S_{vv}(k, t = 0)$$

are superpositions of two lorentzians

$$S_{vv}(k, \omega) = -\text{Im} \left[ \frac{Z_v(D_+)}{\omega + ik^2 D_+} + \frac{Z_v(D_-)}{\omega + ik^2 D_-} \right] S_{vv}(k, t = 0). \quad (8)$$

Their widths  $k^2 D_{\pm}$  are given by the eigenvalues

$$D_{\pm} = \frac{D_{11} + D_{22}}{2} \pm \left[ \left( \frac{D_{11} - D_{22}}{2} \right)^2 + D_{12} D_{21} \right]^{1/2}. \quad (9)$$

The total strength  $Z_v(D_+) + Z_v(D_-)$  is 1 and

$$Z_1(D_+) = Z_2(D_-) = (D_+ - D_{22})(D_+ - D_-)^{-1}. \quad (10)$$

In deriving equation (8) I discarded the remainder ( $v \geq 2$ ) of the infinite set of conserved densities

$$a_{v+1}(\mathbf{k}) = Q_1 \dots Q_v H_0^v \exp(-i\mathbf{k} \cdot \mathbf{r}_0). \quad (11)$$

Properly orthogonalised by projectors

$$Q_v A(\mathbf{k}) = A(\mathbf{k}) - a_v(\mathbf{k}) \langle \delta a_v^*(\mathbf{k}) \delta a_v(\mathbf{k}) \rangle^{-1} \langle \delta a_v^*(\mathbf{k}) \delta A(\mathbf{k}) \rangle$$

they provide a basis to expand any function  $f(H_0) \exp(-i\mathbf{k} \cdot \mathbf{r}_0)$ . Since in this system there is no *a priori* reason to neglect equation (11), it is helpful to assess their influence at least for the special case of a pure hard sphere interaction

$$u_0(r) = \begin{cases} \infty & r \leq \sigma \\ 0 & r > \sigma \end{cases} \quad (12)$$

between particle and scatterers which I will henceforth consider. The above spectra (8) can then be explicitly evaluated and the effect of the slow modes (11) can be quantitatively determined. Furthermore, one can first evaluate the number density correlation function for a particular fixed energy  $H_0 = p_0^2/2m$  and then average that result with the canonical weight  $\sim \exp(-\beta p_0^2/2m)$ .

However, the hard sphere case is somewhat pathological since the particle's path through the scatterer environment is independent of the energy  $H_0$ , the latter two being statistically decoupled. This allows us to express the diffusivities  $D_{v\mu}$  in terms of the self-diffusion constant  $D_{11}$ , since: (i)  $|v_0(t)| = v_0$  is constant in time; and (ii) the cosine of the angle between the velocity directions at time  $t$  and time 0 when averaged over the ensemble of positions  $\mathbf{r}_0$  and  $\{\mathbf{r}_n\}$  depends on time and velocity  $v_0$  only via the distance  $v_0 t$  the particle has travelled in time  $t$ . Measuring the latter in terms of the frequency

$$v \sim v_0 n_s \sigma^{d-1} \quad (13a)$$

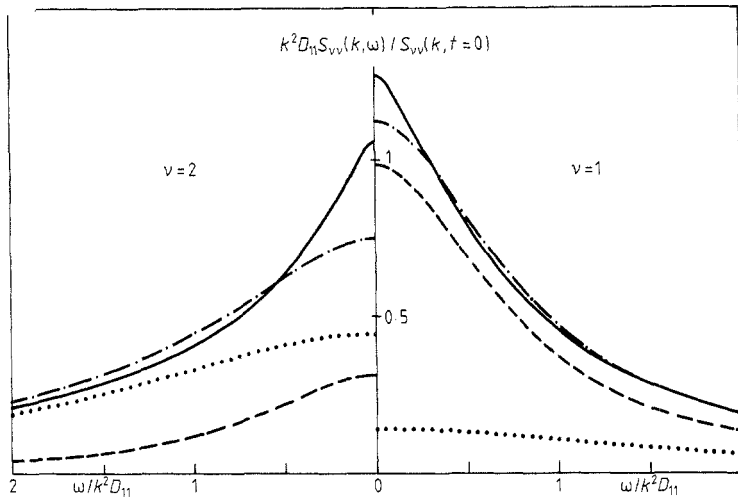
at which a particle of velocity  $v_0$  collides with hard spheres of density  $n_s = N_s/V$ , one finds

$$\frac{1}{d} \left\langle \frac{v_0(\mathbf{t}) \cdot v_0}{v_0^2} \right\rangle_{\mathbf{r}_0, \{\mathbf{r}_n\}} = \psi(tv). \quad (13b)$$

The additional dependence of  $\psi$  on  $n_s$ , on the potential parameters in the statistical weight for  $\{r_n\}$ , and on  $\beta$  if the interbath potential is non-hard sphere, is not displayed here. With equation (13) one obtains  $D_{11} = \langle v_0^2 v^{-1} \rangle \int_0^\infty d\tau \psi(\tau)$ , and inserting  $H_0 = p_0^2/2m$  in equations (6) and (7)

$$D = D_{11} \begin{pmatrix} 1 & (1/k_B T)(1/d) \\ (k_B T/2) & 1 + (3/2d) \end{pmatrix}. \tag{14}$$

The chain curves in figure 1 show the two-mode result (8) for the low  $k, \omega$  autocorrelation spectra of number density and energy density fluctuations in  $d = 3$  dimensions where the eigenvalues of equation (14) are  $D_{\pm}/D_{11} = \frac{5}{4} \pm \sqrt{33/12}$ , together with the contributions from the first (....) and second (-----) lorentzian in equation (8).



**Figure 1.** Contributions to the dimensionless fluctuation spectra (chain curves) of the densities (4) of particle number ( $v = 1$ ) and energy ( $v = 2$ ) stemming from the first (....) and second (-----) Lorentzian in equation (8) as functions of the reduced frequency  $\omega/(k^2 D_{11})$  for  $d = 3$ . The full curve is the corresponding infinite-mode result (18).

In the following the effect of the other modes (11) is discussed. By taking explicitly  $n$  of them into account, one obtains an  $n$  by  $n$  matrix of spectral functions of the form (5). Then the autocorrelation functions are superpositions of  $n$  Lorentzians, e.g.

$$S_{11}^{(n)}(k, \omega) = -\text{Im} \sum_{v=1}^n \frac{Z(y_v)}{\omega + ik^2 D_{11} y_v} \tag{15}$$

$$\simeq -\text{Im} \int_0^\infty dy \frac{\rho(y)Z(y)}{\omega + ik^2 D_{11} y}.$$

Here  $\{y_v; v = 1 \dots n\}$  are the non-degenerate positive temperature-independent eigenvalues of the  $n$  by  $n$  reduced diffusivity matrix  $D/D_{11}$ , the elements of which are easily evaluated (Haus and Lücke 1981). Again the spectral weights  $Z(y_v)$  add up to 1:

$$1 = \sum_{v=1}^n Z(y_v) \simeq \int_0^\infty dy \rho(y)Z(y). \tag{16}$$

For large  $n$  the density  $\rho(y)$  of eigenvalues is practically constant between a maximum ( $y_{\max}$ ) and a minimum ( $y_{\min} \sim n^{-1/2}$ ). The eigenvalue range  $y_{\max} - y_{\min}$  grows slower than  $n$ . Thus  $\rho(y)$  increases with  $n$  and the weight  $Z(y)$  decreases in order to satisfy equation (16). For large  $n$  one obtains (Haus and Lücke 1981)

$$\rho(y)Z(y) = y^{d-1} \exp(-ay^2) / \int_0^\infty dy y^{d-1} \exp(-ay^2) = P(y) \tag{17}$$

i.e. the probability distribution of  $y = v_0 / \langle v_0 \rangle$  with

$$a = \langle v_0 \rangle^2 \beta m / 2 = \left[ \Gamma\left(\frac{d+1}{2}\right) / \Gamma\left(\frac{d}{2}\right) \right]^2.$$

So the low  $k, \omega$  spectra  $S_{11}^{(n)}(k, \omega)$  of number density fluctuations converge for  $n \rightarrow \infty$  towards

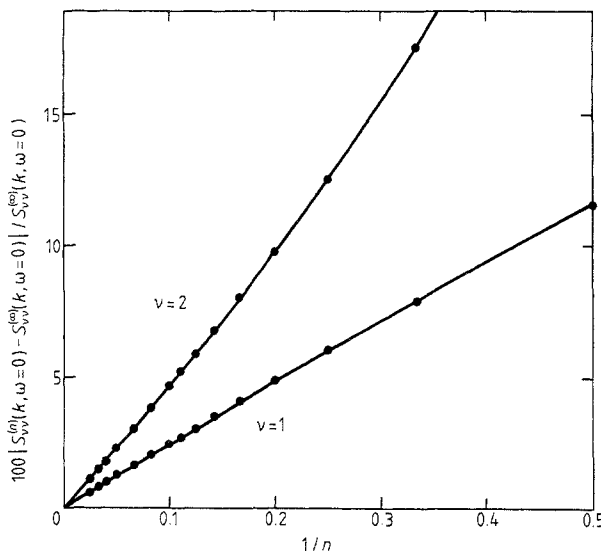
$$S_{11}^{(\infty)}(k, \omega) = -\text{Im} \left\langle \frac{1}{\omega + ik^2 D_{11} v_0 / \langle v_0 \rangle} \right\rangle = \frac{1}{k^2 D_{11}} a [1 - ax^2 \exp(ax^2) E_1(ax^2)]. \tag{18a}$$

The last equality holds for  $d = 3$ .  $E_1$  is the exponential integral function and  $x = \omega / k^2 D_{11}$ . Similarly one obtains

$$S_{22}^{(\infty)}(k, \omega) = -\text{Im} \left\langle \frac{(\delta H_0)^2}{\omega + ik^2 D_{11} v_0 / \langle v_0 \rangle} \right\rangle \tag{18b}$$

which can also be given in terms of  $E_1$ . The two-mode result (8,14) deviates in  $d = 3$  from  $S_{vv}^{(\infty)}(k, \omega)$  (cf full curves in figure 1) by 11.6% and 29.3% respectively at  $\omega = 0$ . There the difference is largest and the convergence (cf figure 2) is slowest.

The zero frequency values of equation (18), e.g.  $k^2 D_{11} S_{11}(k, \omega = 0) = \langle v_0 \rangle \langle v_0^{-1} \rangle$ , are exact, which can be seen as follows. For small wavenumbers the generalised diffusivity



**Figure 2.** Deviation of the  $n$ -mode approximation  $S_{vv}^{(n)}(k, \omega = 0)$  to the zero frequency value of number density ( $v = 1$ ) and energy density ( $v = 2$ ) fluctuations as functions of  $1/n$ . The curves are guides to the eye.

of number density fluctuations evaluated for a fixed energy  $(m/2)v_0^2$  is given by the Laplace transform of the velocity autocorrelation function (13):

$$D_{v_0}(k \rightarrow 0, \omega + i0) = v^{-1}v_0^2\psi\left(\frac{\omega}{v} + i0\right) \\ = iD_{11}\frac{v_0}{\langle v_0 \rangle} \frac{\psi[\omega/\langle v \rangle(\langle v_0 \rangle/v_0) + i0]}{\psi(0)} \quad (19)$$

where  $v/\langle v \rangle = v_0/\langle v_0 \rangle$  was used. Hence the matrix of number density and energy density correlations obtains, by a velocity average over the small  $k$  number density fluctuation spectrum determined for a particular velocity  $v_0$ ,

$$S(k, \omega) = -\text{Im} \left\langle \left[ \omega + ik^2D_{11}\frac{v_0}{\langle v_0 \rangle} \frac{\psi[(\omega/\langle v \rangle)(\langle v_0 \rangle/v_0) + i0]}{\psi(0)} \right]^{-1} \begin{pmatrix} 1 & \delta H_0 \\ \delta H_0 & (\delta H_0)^2 \end{pmatrix} \right\rangle. \quad (20)$$

Obviously the infinite-mode result  $S^{(\infty)}(k, \omega)$  (18) is equivalent to replacing in equation (20) the spectrum of velocity fluctuations by its zero frequency value. If one approximates  $\psi(tv) \sim \exp(-\alpha|t|v)$  with  $\alpha$  taken from computer experiments to be of the order of 1, or if one uses the experimental velocity correlation function, equation (20) gives practically the same result as equation (18) for  $\omega, k^2D_{11} \ll \langle v \rangle$  (Haus and Lücke 1981). For  $\psi(tv) \sim \exp(-\alpha|t|v)$  the average in equation (20) is obtained in terms of  $E_1$  functions.

Unfortunately it is quite difficult to generalise the approach (19, 20) to non-hard sphere interaction potentials, since  $D_{v_0}(k, \omega)$  will then depend on the initial velocity  $v_0 = |v_0(t=0)|$  in a much more complicated way. Also, evaluating  $D_{E_0}(k, \omega)$  in a micro-canonical ensemble for a total energy  $H_0 = E_0$  of the particle in a continuous potential poses problems. Not only will  $D_{E_0}(k, \omega)$  strongly depend on  $E_0$ ; one also has to know the probability density  $\langle \delta(H_0 - E_0) \rangle$ , i.e. the density of states  $n(E_0)$ , in order to evaluate the canonical average (1). In view of these difficulties it seems to be advantageous to use only canonical averages, and to describe low  $k, \omega$  spectra in terms of diffusivities of the conserved modes  $a_v(\mathbf{k})$ . It is reassuring that in the hard sphere system for real  $\omega$  the two-pole approximation (8) is already very close to the infinite mode result  $\langle [\omega + ik^2D_{11}v_0/\langle v_0 \rangle]^{-1} \rangle$ . The latter displays continuously many poles at  $\omega = -i\eta = -ik^2D_{11}v_0/\langle v_0 \rangle$  with infinitesimal residues, adding up for any finite dimension  $d$  to a cut from  $\omega = -i0$  to  $\omega = -i\infty$  across which there is a discontinuity  $2\pi P(\eta/k^2D_{11})/k^2D_{11}$ . Only for  $d \rightarrow \infty$ , where the total spectral intensity  $\langle (\delta H_0)^2 \rangle / \langle H_0 \rangle^2 = 2/d$  of energy density fluctuations and the other modes (11) vanish, when properly normalised one recovers a nice 'hydrodynamic' spectrum. In that limit the  $n \times n$  diffusivity matrix  $D/D_{11}$  has only one  $n$ -fold degenerate eigenvalue  $y = 1$  as a result of the probability distribution  $P(y = v_0/\langle v_0 \rangle)$  (equation (17)) becoming sharply peaked around  $y = 1$ . Thus only for  $d \rightarrow \infty$  are the low  $k, \omega$  fluctuations

$$S_{vv}(k, \omega) \underset{d \rightarrow \infty}{=} -\text{Im} \frac{1}{\omega + ik^2D_{11}} S_{vv}(k, t=0) \quad (21)$$

characterised by only one relaxation rate  $k^2D_{11}$ . As an amusing aside, we note that the modes (11) can be written as products  $a(\mathbf{q})a(\mathbf{k} - \mathbf{q})$  of the two basic conserved densities (4). In real many-body systems, similar products of slow modes destroy the hydrodynamic behaviour below a critical dimension  $d_c$  (in fluids  $d_c = 2$ ) where the volume  $q^{d_c-1}dq$  around the 'dangerous' wavenumber  $q = 0$  becomes sufficiently large. Here any wavenumber  $q$  is 'dangerous' and  $d_c = \infty$ .

For hard sphere potentials the self-diffusion constant

$$D_{11} = \lim_{t \rightarrow \infty} t^{-1} \langle (r_0(t) - r_0)^2 \rangle$$

is independent of energy fluctuations except for a factor  $\langle v_0 \rangle$ , whereas a particle's mean square displacement in a continuous potential depends non-trivially on temperature. In this and in other respects, such a system (Lücke 1981) is dynamically richer than the conventional hard sphere Lorentz model for which, as an example, the problem of vanishing diffusivities is a function of scatterer density only.

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