LONG TIME TAILS FOR THE DIFFUSION OF TAGGED PARTICLES THROUGH A FLUID

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Received 27 February 1973

A simple formalisme is developed to calculate the long time behaviour of the memory kernel for the diffusion of tagged particles through a fluid.

The density $n(\boldsymbol{r}, t)$ and the current $\boldsymbol{j}(\boldsymbol{r}, t)$ of the tagged particles satisfy the conservation law

$$\frac{\partial}{\partial t} n(\boldsymbol{r}, t) = -\operatorname{div} \boldsymbol{j}(\boldsymbol{r}, t) \tag{1}$$

The current is given by

$$\boldsymbol{j}(\boldsymbol{r}, t) = \boldsymbol{v}(\boldsymbol{r}, t)\, n(\boldsymbol{r}, t) - D_0 \operatorname{grad} n(\boldsymbol{r}, t) + \boldsymbol{j}_{\mathrm{R}}(\boldsymbol{r}, t) \tag{2}$$

where $\boldsymbol{v}(\boldsymbol{r}, t)$ is the fluctuating velocity field of the fluid and $\boldsymbol{v}(\boldsymbol{r}, t)\, n(\boldsymbol{r}, t)$ is the corresponding fluctuating convective part of the current, D_0 is the "bare" diffusion coefficient with respect to the moving fluid and $\boldsymbol{j}_{\mathrm{R}}(\boldsymbol{r}, t)$ is the random current. Substitution of eq. (2) into eq. (1) and Fourier transformation of the resulting equation yields

$$(\mathrm{i}\omega - D_0 k^2)\, n(\boldsymbol{k}, \omega) = \mathrm{i}\boldsymbol{k} \cdot (\boldsymbol{v} n)(\boldsymbol{k}, \omega) + \mathrm{i}\boldsymbol{k} \cdot \boldsymbol{j}_{\mathrm{R}}(\boldsymbol{k}, \omega) \tag{3}$$

Note that $\boldsymbol{v}$ can be interpreted as a convolution operator in $\boldsymbol{k}, \omega$ representation. Eq. (3) is a stochastic equation for the density of the tagged particles. The density of the tagged particles is taken sufficiently small so that the velocity fluctuations of the fluid are those of the pure fluid in equilibrium. Furthermore we assume that the average of $\boldsymbol{j}_{\mathrm{R}}$, keeping $\boldsymbol{v}(\boldsymbol{k}, \omega)$ constant for all $\boldsymbol{k}$ and ω, is zero

$$\langle \boldsymbol{j}_{\mathrm{R}}(\boldsymbol{k}, \omega) \rangle_{v} = 0 \tag{4}$$

Taking the same average of eq. (3) one obtains

$$(\mathrm{i}\omega - D_0 k^2)\, \langle n(\boldsymbol{k}, \omega) \rangle_{v} = \mathrm{i}\boldsymbol{k} \cdot \boldsymbol{v} \langle n(\boldsymbol{k}, \omega) \rangle_{v}. \tag{5}$$

It can now be shown that if one averages also over the velocity fluctuations of the fluid that $\langle n(\boldsymbol{k}, \omega) \rangle$ obeys the equation

$$(\mathrm{i}\omega - D(\boldsymbol{k}, \omega) k^2)\, \langle n(\boldsymbol{k}, \omega) \rangle = 0 \tag{6}$$

where the "renormalized" diffusion coefficient is given by

$$(D(\boldsymbol{k}, \omega) - D_0)\, \delta(\boldsymbol{k} - \boldsymbol{k}')\, \delta(\omega - \omega') = k^{-2} \left[\langle \mathrm{i}\boldsymbol{k} \cdot \boldsymbol{v} [1 - \mathrm{i}G\boldsymbol{k} \cdot \boldsymbol{v}]^{-1} \rangle \langle [1 - \mathrm{i}G\boldsymbol{k} \cdot \boldsymbol{v}]^{-1} \rangle^{-1} \right] (\boldsymbol{k}, \omega | \boldsymbol{k}', \omega') \tag{7}$$

with

$$G(\boldsymbol{k}, \omega) = (\mathrm{i}\omega - D_0 k^2)^{-1}. \tag{8}$$

Up to second order in the fluctuations of the fluid velocity and as a function of $\boldsymbol{k}$ and t eq. (7) gives

$$D(\boldsymbol{k}, t) = D_0 \delta(t) - (2\pi)^{-3} k^{-2} \int \mathrm{d}\boldsymbol{k}'\, \boldsymbol{k} \cdot \mathbf{S}(\boldsymbol{k} - \boldsymbol{k}', \omega - \omega') \cdot (\boldsymbol{k} - \boldsymbol{k}')\, G(k', \omega) \tag{9}$$

where translational invariance of the velocity correlation function $\mathbf{S}$ has been used

$$\mathbf{S}(\boldsymbol{k}\,\omega)\,\delta(\boldsymbol{k}-\boldsymbol{k}')\,\delta(\omega-\omega')\equiv\langle \boldsymbol{v}(\boldsymbol{k},\omega)\,\boldsymbol{v}^*(\boldsymbol{k}',\omega')\rangle. \tag{10}$$

We have evaluated $D(\boldsymbol{k},t)$ for all values of $\boldsymbol{k}$ and sufficiently large t using for $\mathbf{S}$ the standard form which follows from linearized hydrodynamics. For $k=0$ the dominant asymptotic term has the well-known form [e.g. 1]

$$D(\boldsymbol{k}=0,t)=\tfrac{2}{3}\,(k_{\mathrm{B}}T/\rho)\,[4\pi t(\nu+D_0)]^{-3/2} \tag{11}$$

where ρ is the mass density and ν the kinematic viscosity of the fluid. If the Landau-Lifschitz linearized hydrodynamic Langevin equations are used ν is the bare viscosity coefficient. It is, however, consistent with our approach to use, in order evaluate $\mathbf{S}(\boldsymbol{k},t)$, the linearized hydrodynamic equations with memory kernel (Mori equations) so that ν should be interpreted as the renormalized viscosity coefficient [2].

Finally we have shown that to assure the validity of the fluctuation-dissipation theorem

$$\langle n(\boldsymbol{k},\omega)\,n^*(\boldsymbol{k},\omega')\rangle=\mathrm{Re}\,[\mathrm{i}\omega-k^2D(\boldsymbol{k},\omega)]^{-1}\,\delta(\boldsymbol{k}-\boldsymbol{k}')\,\delta(\omega-\omega') \tag{12}$$

the random current has to satisfy

$$\boldsymbol{k}\cdot\langle \boldsymbol{j}_{\mathrm{R}}(\boldsymbol{k},\omega)\,\boldsymbol{j}_{\mathrm{R}}^*(\boldsymbol{k}',\omega')\rangle_{\boldsymbol{v}}\cdot\boldsymbol{k}'=D_0k^2\delta(\boldsymbol{k}-\boldsymbol{k}')\,\delta(\omega-\omega')+\tfrac{1}{2}\,\mathrm{i}(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{v}(\boldsymbol{k}-\boldsymbol{k}',\omega-\omega'). \tag{13}$$

This implies that

$$\boldsymbol{k}\cdot\langle \boldsymbol{j}_{\mathrm{R}}(\boldsymbol{k},\omega)\,\boldsymbol{j}_{\mathrm{R}}^*(\boldsymbol{k}',\omega')\rangle\cdot\boldsymbol{k}'=D_0k^2\delta(\boldsymbol{k}-\boldsymbol{k}')\,\delta(\omega-\omega'). \tag{14}$$

We see therefore that due to the bilinear form of eq. (2) the random current for a given velocity field $\boldsymbol{v}(\boldsymbol{k},\omega)$ has no white noise spectrum. It is only upon averaging over the fluctuations in the fluid that the noise spectrum becomes white. As a consequence of eq. (13) it also follows that the random current if assumed to be a Gaussian process at constant fluid velocity field is non Gaussian upon averaging over the fluid velocities [3]. A detailed discussion of the above formalisme will be published in a forth-coming paper.

References

[1] M.H. Ernst, E.H. Hauge and J.M.J. van Leeuwen, Phys. Rev. Lett. 25 (1971) 1254.
[2] R. Zwanzig, Statistical mechanics, Proc. Sixth I.U.P.A.P. Conf. on Statistical mechanics (The University of Chicago Press 1972).
[3] See discussion remarks by R. Kubo and N.G. van Kampen, page 317 of ref. [2].