The long-time fluctuations of a Brownian sphere

1979 J. Phys. A: Math. Gen. 12 1511

(http://iopscience.iop.org/0305-4470/12/9/018)

J. Phys. A: Math. Gen., Vol. 12, No. 9, 1979. Printed in Great Britain

The long-time fluctuations of a Brownian sphere

M Warner

Blackett Laboratory, Imperial College, Prince Consort Road, London SW7 2BZ, UK

Received 17 January 1978, in final form, 2 November 1978

Abstract. Statistical-mechanical problems of principle associated with long-time correlation are discussed using the example of retarded Brownian motion. The well known 'stochastic' solutions are quoted and the fundamental inadequacies of the Fokker–Planck solutions to the problem demonstrated.

An alternative is to adopt Edwards' concept of a 'Lagrangian' phase space with a Langrangian Fokker–Planck equation. Within this extended phase space, problems of history dependence, non-separation of time scales and non-exponential decays are solved *consistently*. In the present case the $t^{-3/2}$ results are trivially re-obtained, but the principles for the solution of more complex problems involving long correlations are illuminated (e.g. time decay of turbulent fluctuations).

Considering the role of the fluctuation–dissipation theorem the character of the asymptotic solution in the Brownian problem is obtained. Examination of this result allows two scattering experiments to be proposed to observe this power-law correlation in velocity.

1. Introduction

The Langevin equation for the velocity $\boldsymbol{u}(t)$ of sphere of radius R moving in a fluid of density ρ and kinematical viscosity ν is

$$m^*\dot{\boldsymbol{u}}(t)+\beta\boldsymbol{u}(t)+\alpha\int_{-\infty}^{t}\frac{\mathrm{d}\tau\,\dot{u}(\tau)}{(t-\tau)^{1/2}}=f(t) \tag{1}$$

where

$$\alpha=6\pi\rho R^2(\nu/\pi)^{1/2}$$
$$\beta=6\pi\rho\nu R$$
$$m^*=m+\tfrac{2}{3}\pi\rho R^3$$

and m is the sphere mass.

For the case of only Stokes drag ($\alpha=0$, $m^*=m$) we have the well known Einstein problem (Chandrasekhar 1943) in which the velocity correlation is exponential:

$$\phi(t)=\langle\boldsymbol{u}(t)\,.\,\boldsymbol{u}(0)\rangle$$
$$=3kT/m\;\mathrm{e}^{-\lambda t}$$

where

$$\lambda=6\pi\nu\rho R/m.$$

Considering inertial effects in the fluid (Landau and Lifshitz 1959) we have ($\alpha\neq0$, $m\to m^*$) a non-Markoff stochastic problem. The velocity correlation is now long-lived and dies like $t^{-3/2}$. This has been observed in hard-sphere systems by Alder and Wainwright (1970), who pictured the longer correlation as resulting from vorticity diffusion out from the sphere. The $t^{-3/2}$ law is obtained straightforwardly in stochastic approaches (see Giterman and Gertsenshtein 1966, Zwanzig and Bixon 1970, or for a review, Pomeau and Reisibois 1975). It is important to notice that the random force $f(t)$ must obey the fluctuation–dissipation (FD) theorem (Kubo 1966). Hence in Fourier space (with ω conjugate to t) we define $h(\omega)$ by

$$h(\omega) = \langle f(\omega) \,.\, f(-\omega) \rangle$$

where $h(\omega)$ must satisfy

$$h(\omega) = 2m^* \operatorname{Re}[\xi(\omega)]\phi(t=0)$$

where $\xi(\omega)$ is the frequency-dependent dissipation term implied in (1). $\phi(t=0)$ is $3kT/m^*$ by equipartition (m^* since we consider the bare sphere plus the effective mass enhancement from the fluid to be one mode).

$\xi(\omega) = \beta$ for the Stokes case. The extra coherency introduced into f in the $\alpha \neq 0$ case gives

$$h(\omega) = 6kT(\beta + \alpha\gamma|\omega|^{1/2}) \tag{2}$$

with $\gamma = (-\frac{1}{2})!/\sqrt{2}$.

The diffusion constant is unaltered (Hinch 1975) by the introduction of the inertial terms into the hydrodynamics and hence the long-time behaviour of the position correlation function $w(t)$ is unchanged:

$$\begin{aligned} w(t) &= \langle (\boldsymbol{R}(t) - \boldsymbol{R}(0))^2 \rangle \\ &= 6Dt \\ D &= kT/m\lambda. \end{aligned} \tag{3}$$

In § 2 we shall discuss the statistical-mechanical problems in the analysis of such motion. A phase space is developed following Edwards (1964), in which we can use the Fokker–Planck (FP) formulation. In § 3 the consequences for light and neutron scattering are discussed. The difficulties of measuring this effect directly by light scattering are shown and an indirect method is suggested as an alternative.

2. Statistical-mechanical implication

The treatment of the Einstein problem within statistical mechanics is via the Fokker–Planck equation

$$[(\partial/\partial t) - D_{\boldsymbol{u}}]P(\boldsymbol{u}, t) = 0 \tag{4}$$

where $D_{\boldsymbol{u}}$ is the diffusion operator and $P(\boldsymbol{u}, t)$ the time-dependent probability distribution function for $\boldsymbol{u}$.

A derivation of (4) from a master equation (Chandrasekhar 1943) requires a separation of time scales between the variables $f(t)$ and $\boldsymbol{u}(t)$. That is, on the time scale of correlations of $\boldsymbol{u}(t)$, $f(t)$ must appear to be delta-correlated.

This can be interpreted physically as follows. Equation (4) tells us that the distribution P 'drives' the dynamics. The diffusion operator in (4) is

$$D_{\boldsymbol{u}} = \frac{\beta kT}{m^2}\frac{\partial}{\partial \boldsymbol{u}}\left(\frac{\partial}{\partial \boldsymbol{u}} + \frac{m}{kT}\boldsymbol{u}\right)$$

which for equilibrium ($\partial/\partial t = 0$) gives the Maxwell distribution

$$P_{\text{eq}}(\boldsymbol{u}) \sim \exp(-mu^2/2kT).$$

Small deviations away from $P_{\text{eq}}(\boldsymbol{u})$ give a finite result when operated on by D, and hence provide the dynamics. In a microscopic sense equilibration is reached by the action of the forces $f(t)$, and over times long compared with the f correlation time we can consider states of quasi-equilibrium. A free energy is hence defined, and can be considered as giving rise to a 'thermal force' driving the system back to equilibrium. We additionally note that (4) has a simple pole structure,

$$(\mathrm{i}\omega + D_{\boldsymbol{u}})P(\boldsymbol{u}, \omega) = 0, \tag{4'}$$

and hence the correlation functions have a simple exponential behaviour in time. This is not the case in the present problem.

What one must not do in the framework of (4) is ask questions about time development over times short compared with the equilibration of P (that is, when there is no thermal force). Hence if the correlation of f is long on a hydrodynamic time scale (that is of $\boldsymbol{u}$) then (4) breaks down altogether. Here we wish to generalise the FP equation to non-exponential time decays where the above theory fails. (The failure of the above approach has been noted by other authors—see Fox (1977) for a different viewpoint. Fox notes that the non-Markoffian nature of the Langevin equation causes one to lose the essential FP character of equations describing diffusion in velocity space.)

We generalise the above by noting that the conventional phase space is Hamiltonian. $\boldsymbol{u}$ is not $\boldsymbol{u}(t)$ and P is only $P(\boldsymbol{u}, t)$. (This is seen when one looks at the definition of P as

$$P(\boldsymbol{u}, t) = \langle \delta(\boldsymbol{u} - \boldsymbol{U}(t)) \rangle$$

where $\boldsymbol{U}(t)$ is an actual trajectory of the particle and one averages over the ensemble of particles and forces f.) For f delta-correlated the problem is Markoff (history independent) and the instaneous phase space is appropriate. This is, however, the very point of inadequacy in the present problem where $\boldsymbol{U}(t)$ depends on $\boldsymbol{U}(t')$ (t' some earlier time) and we must follow the system in time in order to handle the history dependence.

We thus take a Lagrangian phase space $\boldsymbol{u}(t)$ with a distribution function $P(\boldsymbol{u}(t), t)$. The phase space is now extended since it covers each instant in time and problems become functional in nature. In the turbulence problem Edwards calls this 'Lagrangian statistical mechanics'. Mazo (1971) and Chow and Hermans (1972) take an opposite view in which they put a time label on derivatives taken in a conventional Hamiltonian phase space: $(\partial/\partial u)|_t$. This is not within the philosophy of Kirkwood 'plateau values'.

Phase-space variables $\boldsymbol{u}(t)$ will be carefully distinguished from stochastic variables $\boldsymbol{U}(t)$. For a definite system we have (on Fourier transforming (1))

$$(\mathrm{i}\omega m^* + \beta + \mathrm{i}\alpha\gamma\omega/|\omega|^{1/2})\boldsymbol{U}(\omega) - \boldsymbol{f}(\omega) = 0. \tag{1'}$$

The probability of finding this definite value in phase space is

$$P(\boldsymbol{u}(\omega)) = \delta(\boldsymbol{u}(\omega) - \boldsymbol{U}(\omega)). \tag{5}$$

An equation for P is then

$$XP = 0 \tag{6}$$

where X is the left-hand side of (1′). This is an equation for each frequency ω. One can add together the infinity of equations (6) in such a way that the moments of (6) are preserved:

$$\int d\omega\,(\delta/\delta \boldsymbol{u}(\omega))\{[i\omega m^* + \beta + (i\alpha\gamma\omega/|\omega|^{1/2})]\boldsymbol{u}(\omega) - \boldsymbol{f}(\omega)\}P(\boldsymbol{u}(\omega)) = 0. \tag{7}$$

This 'Lagrangian Liouville equation' can be reduced to a FP equation by averaging over all forms of the random force $f(\omega)$. We take the force to be truly random with arbitrary correlation:

$$P(f(t)) \sim \exp(-\int dt\, dt' \tfrac{1}{2} f(t) h^{-1}(t-t') \cdot f(t')), \tag{8}$$

where, as before,

$$\langle f(t) \cdot f(t')\rangle = h(t-t').$$

Averaging of (7) over (8) is trivial (Edwards 1964) and gives

$$\int d\omega\,(\delta/\delta \boldsymbol{u}(\omega))[(h(\omega)/\Omega^*(\omega))(\delta/\delta \boldsymbol{u}(-\omega)) + \Omega(\omega)\boldsymbol{u}(\omega)]\langle P\rangle = 0 \tag{9}$$

where $\langle P\rangle$ denotes the distribution function averaged over f and

$$\Omega(\omega) = i\omega m^* + \beta + i\alpha\gamma\omega/|\omega|^{1/2}.$$

We call this a Lagrangian FP equation.

The second moment of (9) is the correlation function

$$\phi(\omega) = h(\omega)/\Omega(\omega)\Omega^*(\omega). \tag{10}$$

In the simple pole case the full upper- and lower-half-plane behaviour is presented by Ω and Ω^* respectively (giving the Einstein correlation functions). In the non-Markoff case the singular nature of Ω and h will give the non-exponential (in our case $t^{-3/2}$) behaviour.

Thus the Lagrangian FP equation overcomes the usual conceptual obstacles involved in 'non-separation of time scales' problems in irreversible thermodynamics. It presents an arguably simpler alternative to the memory function/generalised Langevin techniques otherwise developed for non-Markoff systems. The method also has the conceptual advantage and appeal that it extends the well known *conventional* apparatus of phase space and thus the derivation of the FP equation closely follows, say, Chandrasekhar (1943). The non-exponential behaviour occurs in a natural and functionally simple way as is seen in equation (10).

The analysis from equation (10) to get the autocorrelation function ϕ is easily completed below. ϕ becomes

$$\phi(\omega) = 6kT/\beta - 6kT\alpha/\alpha|\omega|^{1/2}/\beta^2 + \frac{12kT\alpha\gamma}{\beta^3}\left(\frac{5\alpha^2\gamma^2}{\beta} - m^*\right)|\omega|^{3/2} + \dots \tag{11}$$

(with the first term the usual $\omega = 0$ result of the Einstein model confirming that D is unaltered).

The long-time behaviour is dominated by the singularities in the ω plane that are closest to the origin (Lighthill 1975.). Hence back Fourier transformation of the generalised functions gives immediately the $t^{-3/2}$ law. It is also interesting to transform more terms in (11) to see that ϕ involves $t^{-3/2}$, $t^{-5/2}$, . . .:

$$\phi(t) \sim \frac{6kT\alpha\gamma^2}{2\pi\beta^2} t^{-3/2} - \frac{18kT\alpha\gamma^2}{2\pi\beta^3}\left(\frac{5\alpha^2\gamma^2}{\beta} - m^*\right) t^{-5/2} + \dots .$$

One can also get an estimate of when the $t^{-3/2}$ term dominates over other power-law dependence. This is after times t_0' where

$$\begin{aligned} t_0' &= 3|5\alpha^2\gamma^2/\beta - m^*|/\beta \\ &= \frac{1}{2\nu\pi R\rho}|15\pi R^3\rho - m^*|. \end{aligned} \tag{12}$$

For spheres of density ρ_s, which is of the order of ρ, one has

$$t_0' = 13R^2/2\nu$$

and for $\rho_s \gg \rho$ one has

$$t_0' = R^2[4(\rho_s/\rho) - 43]/6\nu.$$

3. Consequences for scattering

3.1. Light scattering

We now return to the position autocorrelation function $w(t)$:

$$w(t) = \langle [\boldsymbol{R}(t) - \boldsymbol{R}(0)]^2 \rangle.$$

Using the stationarity of the random process one gets (on doubly differentiating)

$$\ddot{w}(t) = 2\phi(t).$$

The three functions $\ddot{w}(t)$, $\dot{w}(t)$ and $w(t)$ are plotted schematically in figures 1(*a*)–(*c*).

In figure 1(*a*) we see that the hydrodynamic effects lead to long-time modifications to the Einstein form. After two integrations we see in figure 1(*c*) that the hydrodynamic effects lead to modifications in the short-time behaviour. (The long-time behaviour is

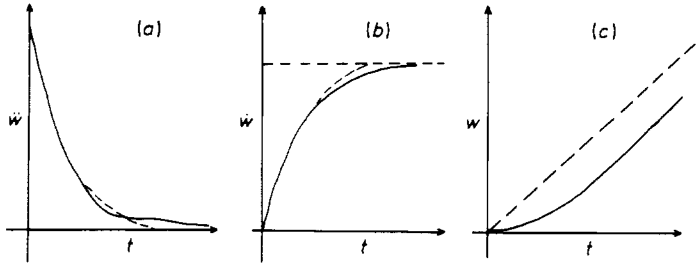

Figure 1. Correlation functions (*a*) $\ddot{w}$, (*b*) $\dot{w}$ and (*c*) w for Brownian motion. The broken curves in (*a*) and (*b*) are the Einstein result, and in (*c*) the line $6Dt$.

$w(t) = 6Dt - c$ and the constant c, being the deviations from the broken curves, is insignificant at long times.)

In a dynamical light-scattering experiment the time-scattering function is commonly measured ($\boldsymbol{k}$ is the scattering vector):

$$S(\boldsymbol{k}, t) = \langle N^{-1} \sum_{ij} \exp[\mathrm{i}\boldsymbol{k} \cdot (\boldsymbol{R}i(t) - \boldsymbol{R}j(0))]\rangle.$$

For a sufficiently dilute solution of scatterers this reduces to

$$S(\boldsymbol{k}, t) = \langle \exp[\mathrm{i}\boldsymbol{k} \cdot (\boldsymbol{R}(t) - \boldsymbol{R}(0))]\rangle$$

where $\boldsymbol{R}(t)$ is the coordinate of the scatterer. Averaging one gets

$$S(\boldsymbol{k}, t) = \exp(-\tfrac{1}{6}k^2 w(t)).$$

Hence one cannot observe ϕ *directly* by light scattering and it is clear that an analysis of the shape of $S(\boldsymbol{k}, t)$ at short times will be necessary to detect 'hydrodynamic' correlation.

There will be 'rounding' in $S(\boldsymbol{k}, t)$ as seen from

$$\ddot{S}(\boldsymbol{k}, t) = \tfrac{1}{6}k^2(\tfrac{1}{6}k^2 \dot{w}^2(t) - \ddot{w}(t)) \exp(-\tfrac{1}{6}k^2 w(t)) \tag{13}$$

(see figure 2 for a sketch of this). Rounding can be caused by either (i) finite velocity correlation over times t_0 as seen in the Einstein model or (ii) longer-lived correlation due to hydrodynamic effects. We suggest an indirect experiment to distinguish between the two effects.

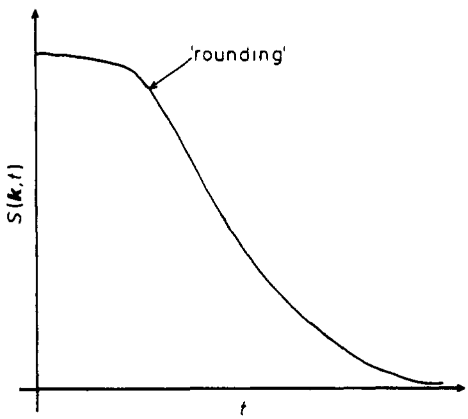

Figure 2. The intermediate scattering function $S(\boldsymbol{k}, t)$ showing 'rounding'.

3.1.1. The Einstein model. From (13) we have $\ddot{S} < 0$ for $\frac{1}{6}k^2\dot{w}^2 < \ddot{w}$. Using the Einstein result $\ddot{w} = (6kT/m)\,\mathrm{e}^{-\lambda t}$ we get $\ddot{S} < 0$ for times $t < t_0''$,

$$t_0'' = -\lambda^{-1} \ln\left(\frac{2\theta + 1 - (4\theta + 1)^{1/2}}{2\theta}\right)$$

with $\theta = 6kTk^2/m\lambda^2$. For θ small this gives us

$$t_0'' = -\lambda^{-1} \ln(\theta) \sim -2\lambda^{-1} \ln(k)$$

and this governs the boundary of the rounded region of $S(\boldsymbol{k}, t)$ as $\boldsymbol{k}$ varies.

3.1.2. The hydrodynamic model. Examination of figures 1 show that it is possible to satisfy $\frac{1}{6}k^2/\dot{w}^2(t) < \ddot{w}(t)$ for much longer times since $\ddot{w}(t)$ remains large longer than in the Einstein case. Hence we would expect to observe rounding in $S(\boldsymbol{k}, t)$ for much longer times, t_0''' say.

It is possible to estimate t_0''' by noticing that the scales in figures 1(*a*) and 1(*b*) are very different. In fact, comparing $\ddot{w}(t=0)$ with $\frac{1}{6}k^2\dot{w}^2(t=\infty)$, that is with $6D^2k^2$, we have

$$6kT/m : \tfrac{1}{6}(6kT/m\lambda)^2k^2 \sim 1 : 10^{-5}$$

(for, say, $1\,\mu$m particles and $k \sim 2\times10^{-6}$ m). Thus the error in taking the asymptotic value for $\dot{w}(t)$ will be small and we hence estimate for t_0'''

$$At_0'''^{-3/2} = 6k^2D^2 \qquad t_0''' = (A/6D^2)^{2/3}k^{-4/3}$$

instead of the logarithmic variation predicted by the Einstein theory for t_0'' (where $A = 6kT\alpha\gamma^2/2\pi\beta^2$ is taken from the expression following (11)).

Experimentally one should decide where the rounding finishes and rather plot this as a function of $\boldsymbol{k}$. This is in contrast to the more exacting curve-fitting procedure of Boon and Bouiller (1976), where the effect has to be seen after the two integrations involved in getting from ϕ to w. Some typical numbers are presented in the appendix.

3.2. Neutron scattering

Here one more commonly observes in the frequency domain. An incoherent cross section is of interest since we wish to follow the correlation of one particle with itself. That is

$$S_{\text{incoh}}(\boldsymbol{k}, \omega) = \int dt \langle \exp[i\boldsymbol{k}\cdot(\boldsymbol{R}(t) - \boldsymbol{R}(0))]\rangle \exp(-i\omega t)$$

This classical picture ignores recoil and is reasonable in a Brownian regime. A suitable system would be a heavy incoherent scatterer dissolved in a coherently scattering fluid. For example, an organic gold complex with hydrogen present in CS_2 would give excellent contrast and a mass ratio of several hundred.

Returning to (13), letting $k \to 0$ and Fourier transforming one gets

$$\omega^2 S_{\text{incoh}}(\boldsymbol{k}, \omega) = \tfrac{1}{6}k^2 \int \exp(-i\omega t) 2\phi(t) \exp(-\tfrac{1}{6}k^2 w(t)).$$

Further, if k is small enough, we can ignore $\frac{1}{6}k^2 w(t)$ at times where $\phi(t)$ still gives a contribution and we get

$$\phi(\omega) = \lim_{k\to0} 3\omega^2 S_{\text{incoh}}(\boldsymbol{k}, \omega)/k^2.$$

Hence one could expect to observe the singular behaviour of ϕ by going to low enough k and frequencies $\omega < \omega_0' \sim 2\pi/t_0'$. Care has to be taken that for a given ω, k is low enough that the conditions for the above derivation to hold are met. The fact the solution (11) for ϕ has several known terms in it enables one to estimate where to look experimentally. Lack of this estimate has hitherto held up the planning of such

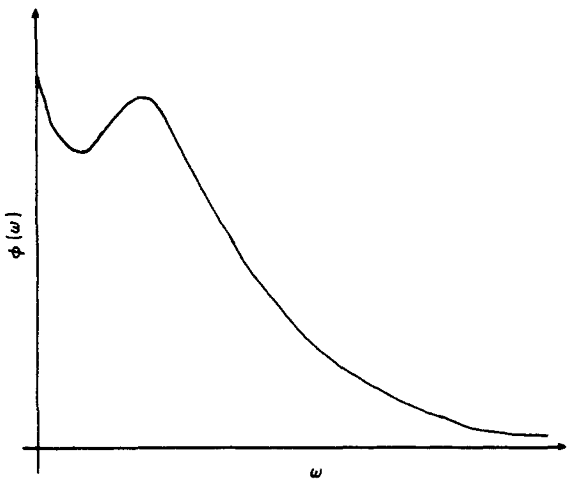

Figure 3. The expected form of $\phi(\omega)$ from neutron scattering.

experiments. Insertion of typical numbers suggest this experiment would be very difficult.

4. Conclusions

We have only discussed briefly the retarded Brownian motion problem within the generalised Langevin formalism. It is important, however, to realise the significance of the fluctuation–dissipation theorem and the role of the enhanced mass m^*. We show that the consideration of these and the use of generalised Fourier analysis provide a simple estimate of when the $t^{-3/2}$ term is dominant in ϕ and also gives the other powers of t involved in the solution. This information appears to be of interest in the planning of a neutron experiment.

The limitation of conventional FP transport theory to regimes where one has time-scale separation and exponential decays is pointed out. As an alternative to this formalism one can use Edwards' generalisation of phase space to a 'Lagrangian phase space'. This retention of the concept of phase space in a generalised and powerful form allows us to generalise the FP formalism in which we have the possibility of non-exponential decays. In fact, the method presents in a direct way the singularities which are responsible for the interesting behaviour. It is envisaged that such a formalism is required more generally to allow FP transport theory to move away from the limitations of simple pole behaviour.

It is hoped that scattering experiments which have hitherto been rather inconclusive in observations of this effect will now proceed by the indirect method suggested. We expect the experiments to be difficult to perform.

Acknowledgments

The author thanks Professor N H March for many interesting discussions in this field. He also thanks Professor S F Edwards for introducing him to the problems of nonlocal transport theory and Dr E J Hinch for the reference to his work.

Appendix

For the case of light scattering from polystyrene spheres in water we present some typical experimental numbers.

Water: $\nu = 10^{-6}\,\mathrm{m^2\,s^{-1}}$;

polystyrene: $R = 10^{-6}$ m, $\rho = 10^3\,\mathrm{kg\,m^{-3}}$. Hence

$$\lambda = 5\times10^6\,\mathrm{s^{-1}} \qquad t_0 = 2\times10^{-7}\,\mathrm{s}(=1/\lambda) \qquad D = 2\times10^{-13}\,\mathrm{m^2s^{-1}}$$

$$(\text{for } T = 300\,\mathrm{K}).$$

The scattering vector is given by

$$k = 4\pi \sin(\tfrac{1}{2}\theta)/\lambda_0$$

where λ_0, the wavelength, is 7000 Å, say. θ is the scattering angle. For a low-angle experiment we have

$$k \sim 2\times10^6\,\mathrm{m^{-1}} \qquad t_0'' = -\lambda^{-1}\ln(kTk^2/m\lambda^2)$$

$$\sim 10\lambda^{-1}.$$

The time t_0' over which the $t^{-3/2}$ tail shows in ϕ is

$$t_0' \sim 29t_0 \sim 5{\cdot}8\times10^{-6}\,\mathrm{s}.$$

The time $t_0''' = (A/D^2)^{2/3}k^{-4/3}$ for the hydrodynamic rounding in $S(\boldsymbol{k}, t)$ is

$$t_0''' \sim (10^2, 10^3)t_0' \sim 10^{-4}\,\mathrm{s}$$

(depending on the values of k). The different effects seem to be well separated in their time scales.

References

Alder B and Wainwright T 1970 *Phys. Rev.* A **1** 18
Boon J P and Bouiller A 1976 *Phys. Lett.* **55A** 391
Chandrasekhar S 1943 *Rev. Mod. Phys.* **15** 1
Chow T S and Hermans J J 1972 *J. Chem. Phys.* **56** 3150
Edwards S F 1964 *J. Fluid Mech.* **18** 239
Fox R F 1977 *J. Math. Phys.* **18** 2331
Giterman M Sh and Gertsenshtein M E 1966 *Sov. Phys.-JETP* **23** 722
Hinch E J 1975 *J. Fluid Mech.* **72** 499
Kubo R 1966 *Rep. Prog. Phys.* **29** 255
Landau L D and Lifshitz E M 1959 *Fluid Mechanics* (Reading, Mass: Addison-Wesley) ch II
Lighthill M J 1975 *Introduction to Fourier Analysis and Generalised Functions* (Cambridge: Cambridge University Press)
Mazo R M 1971 *J. Chem. Phys.* **54** 3712
Pomeau Y and Reisibois P 1975 *Phys. Rep.* **19** 63–139
Zwanzig R and Bixon M 1970 *Phys. Rev.* A **2** 2005