Journal of Statistical Physics, Vol. 87, Nos. 5/6, 1997

Generalized Irreducible Memory Function

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Received January 23, 1996; final April 15, 1996

In a previous paper we presented a general scheme to reduce the memory function in nonequilibrium statistical physics for purely dissipative cases with detailed balance. Here we simplify and generalize further this scheme to include cases other than purely dissipative ones. As an illustration we discuss simple dense fluids.

KEY WORDS: Memory function; freezing; nonequilibrium.

1. INTRODUCTION

The irreducible memory function was introduced by Cichocki and Hess[1] in the theory of colloidal suspension and its usefulness as a starting point for approximations was recognized. We gave a formal recipe for constructing irreducible memory functions for general dissipative stochastic systems with detailed balance.[2] In this article we show that this recipe can be further extended to include the case's which are no longer purely dissipative, and can also contain memory effects. In Section 2 we present a general formulation where we make extensive use of the projector technique in nonequilibrium statistical physics.[3] In Section 3 we illustrate the general approach for the case of dense fluids. This also shows the way to deal with purely nondissipative cases, for which direct application of the recipe of Section 2 does not lead to useful results. The paper is concluded in Section 4.

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0022-4715/97/0600-0981$12.50/0

2. IRREDUCIBLE MEMORY FUNCTION

Here we consider an evolution equation of general type with memory for the distribution function or functional $D(a, t)$ which reads as follows:

$$\frac{\partial}{\partial t} D(a, t) = \int_0^t dt' \, \omega(a, t-t') \, D(a, t') \tag{1}$$

where a is a set of variables or fields that describe a state of the system and $\omega(a, t-t')$ is the time evolution operator with memory which acts on a. A special case of Eq. (1) without memory effects is the well-known kinetic Ising model. The following formal manipuration works as long as the "first moment" $E(z)$ defined below by Eq. (15) does not identically vanish. However, the true value of the formal results can be judged only by applications to various concrete situations.

For our purpose it is convenient to work with the Laplace transforms, which are denoted with superscripts L. That is, for any $X(a, t)$ we have

$$X^L(a, z) = \int_0^\infty dt \, e^{-zt} X(a, t) \tag{2}$$

Thus (1) is written, denoting $\omega^L(a, z)$ by $\Omega(a, z)$, as

$$[z - \Omega(a, z)] \, D^L(a, z) = D(a, 0) \tag{3}$$

Hence the formal solution of (3) is

$$D^L(a, z) = [z - \Omega(a, z)]^{-1} \, D(a, 0) \tag{4}$$

In the following we often replace the argument a simply by a dot, which may even be suppressed when confusion does not arise. We also assume that we have the equilibrium distribution $D_e(a)$ which is a stationary distribution of (1). Now, let $A(a)$ be a physical quantity expressed as a function or functional of a such that its equilibrium average vanishes and its equilibrium variance is normalized to unity. That is, denoting an equilibrium average by an angular bracket and complex conjugate by an asterisk,

$$\langle A(a) \rangle = \langle A^*(a) \rangle = 0, \qquad \langle A(a) \, A^*(a) \rangle = 1$$

We then define a correlator $C(t)$ by

$$C(t) = \langle A(\cdot, t) \, A^*(\cdot, 0) \rangle \equiv \int da \, A(a) \, D_A(a, t) \tag{5}$$

where $D_A(a, t)$ satisfies (1) with the initial condition

$$D_A(\cdot, 0) = A^*(\cdot)\, D_e(\cdot) \tag{6}$$

Here we introduce the bra and ket notation by

$$\langle X(a)... = \int da\, X(a)... \tag{7}$$

$$...X(a)\rangle = \int ...X(a)\, D_e(a)\, da \tag{8}$$

Thus $\langle X(a)\rangle$ defines the equilibrium average of $X(a)$.

The normalization of $D(\cdot, t)$ and the stationarity of $D_e(\cdot)$ then require

$$\langle \Omega(z) = \Omega(z)\rangle = 0 \tag{9}$$

where $X(a)$ can be an operator. We also define a projector $\mathscr{P}$ acting in the space of the state vectors (7) and (8) by

$$\mathscr{P} = A^*\rangle\langle A \tag{10}$$

Then we readily find in view of $\langle A\rangle = \langle A^*\rangle = 0$

$$C^L(z) = \langle A[z - \Omega(z)]^{-1} A^*\rangle = \langle A\mathscr{P}[z - \Omega(z)]^{-1}\mathscr{P}A^*\rangle \tag{11}$$

Here we employ the following operator identity[4]:

$$\mathscr{P}[z - \Omega(z)]^{-1}\mathscr{P} = \{z - \mathscr{P}\Omega(z)\mathscr{P} - \mathscr{P}\Omega(z)[z - \mathscr{Q}\Omega(z)]^{-1}\mathscr{Q}\Omega(z)\mathscr{P}\}^{-1}\mathscr{P} \tag{12}$$

with $\mathscr{Q} \equiv 1 - \mathscr{P}$ a complementary projector.[2] Note that an operator sandwiched between two $\mathscr{P}$ is no longer an operator. That is, for any operator X we have

$$\mathscr{P}X\mathscr{P} = \langle AXA^*\rangle\, \mathscr{P} \tag{13}$$

Therefore, (11) is transformed into

$$C^L(z) = [z - E(z) - M(z)]^{-1} \tag{14}$$

[2] If we wish, $\mathscr{Q}$ can be replaced by $\mathscr{Q} \equiv 1 - \rangle\langle - \mathscr{P}$ since $\rangle\langle$ juxtaposed to $\Omega(z)$ vanishes by (9).

with

$$E(z) \equiv \langle A\Omega(z)\, A^* \rangle \tag{15}$$

$$M(z) \equiv \langle A\Omega(z)[z - \mathcal{Q}\Omega(z)]^{-1}\, \mathcal{Q}\Omega(z)\, A^* \rangle \tag{16}$$

Equations (14)–(16) provide a generalization of the usual memory function formalism where $E(z)$ is the so-called first moment frequency, which now depends on z, and $M(z)$ is the memory function.

The next step is to split $\Omega(z)$ into two parts:

$$\Omega(z) = \Omega_0(z) + \Omega_1(z) \tag{17}$$

where

$$\Omega_0(z) \equiv \Omega(z)\, A^* \rangle\, E(z)^{-1} \langle A\Omega(z) \tag{18}$$

which also defines $\Omega_1(z)$. Noting that $\mathcal{Q}\Omega(z)$ in the middle of (16) can be replaced by $\mathcal{Q}\Omega(z)\,\mathcal{Q}$, we define

$$\hat{\Omega}(z) \equiv \mathcal{Q}\Omega(z)\,\mathcal{Q} \tag{19}$$

$$\hat{\Omega}_j(z) \equiv \mathcal{Q}\Omega_j(z)\,\mathcal{Q}, \qquad j = 0, 1 \tag{20}$$

Then, (16) can be transformed using another operator identity as follows:

$$[z - \hat{\Omega}(z)]^{-1} = [z - \hat{\Omega}_1(z)]^{-1} + [z - \hat{\Omega}(z)]^{-1}\, \hat{\Omega}_0(z)[z - \hat{\Omega}_1(z)]^{-1} \tag{21}$$

Thus we find

$$M(z) = M^{\mathrm{ir}}(z) + M(z)\, E(z)^{-1}\, M^{\mathrm{ir}}(z) \tag{22}$$

where $M^{\mathrm{ir}}(z)$ is the irreducible memory function defined by

$$M^{\mathrm{ir}}(z) \equiv \langle A\Omega(z)[z - \hat{\Omega}_1(z)]^{-1}\, \mathcal{Q}\Omega(z)\, A^* \rangle \tag{23}$$

$M(z)$ is then expressed in terms of $M^{\mathrm{ir}}(z)$ as

$$M(z) = [1 - M^{\mathrm{ir}}(z)\, E(z)^{-1}]^{-1}\, M^{\mathrm{ir}}(z) \tag{24}$$

Hence $C^L(z)$ becomes[3]

$$C^L(z) = \{z - E(z)[1 - E(z)^{-1}\, M^{\mathrm{ir}}(z)]^{-1}\}^{-1} \tag{25}$$

[3] Here we wish to correct two errors in Ref. 2. In the line next to Eq. (2.29), "neglected" should read "replaced." On the lhs of Eq. (2.44), $[1 - E_A^{-1} M_A^{\mathrm{ir}}(z)]^{-1}$ should be replaced by $[1 - E_A^{-1} M_A^{\mathrm{ir}}(z)]$.

This result generalizes that of Ref. 2. for purely dissipative cases and the derivation is simplified as well. As in the previous case, utility of (24) is most evident when we deal with near freezing. That is, $C(t)$ develops a very long tail in which $C(t)$ approaches a finite value, say f, at sufficiently long times, although $C(t)$ may eventually decay to zero at infinity. Then, for sufficiently small values of $|z|$, which corresponds to the time window of near freezing, we will find

$$C^L(z) \cong f/z \tag{26}$$

and hence

$$E(z) + M(z) \cong [(f-1)/f]\, z \tag{27}$$

and

$$M^{\text{ir}}(z) \cong [f/(f-1)]\, E(z)^2/z \tag{28}$$

If this is the case, any sensible approximation for $E(z)$ and especially for $M(z)$ to describe near freezing must be such that the delicate cancellation of $E(z)$ and $M(z)$ as $|z| \to 0$ is guaranteed. On the other hand, when $E(z)$ always remains finite, (22) simply requires $M^{\text{ir}}(z)$ to tend to diverge for small $|z|$. Thus, even a crude approximation for $M^{\text{ir}}(z)$ leading to its divergence serves our purpose.

3. CLASSICAL FLUIDS

We illustrate the foregoing general formalism for the case of a classical fluid consisting of N particles of mass m. We then use the notations $\mathbf{r}^N$ and $\mathbf{p}^N$ to denote the sets of the position vectors $\mathbf{r}_1, \ldots, \mathbf{r}_N$ and the momentum vectors $\mathbf{p}_1, \ldots, \mathbf{p}_N$ of the N particles, respectively. We now choose

$$A = n_{\mathbf{k}}/\sqrt{NS(k)} \tag{29}$$

where $n_{\mathbf{k}}$ is the Fourier component of the particle number density fluctuation expressed in terms of $\mathbf{r}^N$, and $S(k)$ is the usual scattering structure function:

$$S(k) = \langle |n_{\mathbf{k}}|^2 \rangle / N \tag{30}$$

We start from the Liouville equation for the N-particle phase space distribution function $\hat{D}_N(t) \equiv \hat{D}_N(\mathbf{r}^N, \mathbf{p}^N, t)$ as follows:

$$\frac{\partial}{\partial t} \hat{D}_N(t) = L_N \hat{D}_N(t) \tag{31}$$

with $L_N \equiv L(\mathbf{r}^N, \mathbf{p}^N)$ the Liouville operator. We note that the Laplace transform of the correlator $C(t)$ takes the form, using the bra and ket notaton introduced in the preceding section,

$$C^L(z) = \langle A(z-L_N)^{-1} A^* \rangle = \langle A\mathscr{P}(z-L_N)^{-1} \mathscr{P}A^* \rangle$$
$$= \langle A\mathscr{P}\hat{\mathscr{P}}(z-L_N)^{-1} \hat{\mathscr{P}}\mathscr{P}A^* \rangle \qquad (32)$$

where $\mathscr{P}$ is the projector defined by (10). Another projector $\hat{\mathscr{P}}$, which projects out momenta, is defined for any phase space function $\hat{X}_N$ by

$$\hat{\mathscr{P}}\hat{X}_N = \Phi_N(\mathbf{p}^N) \int d\mathbf{p}^N \hat{X}_N \qquad (33)$$

where $\Phi_N(\mathbf{p}^N)$ is the normalized Maxwell momentum distribution function.

Let us first deal with $\hat{\mathscr{P}}(z-L_N)^{-1} \hat{\mathscr{P}}$. Using the operator identity (12) where $\mathscr{P}$ and $\Omega(z)$ there are replaced by $\hat{\mathscr{P}}$ and L_N, respectively, we find, as will be briefly explained below,

$$\hat{\mathscr{P}}(z-L_N)^{-1} \hat{\mathscr{P}} = [z-\Omega(z)]^{-1} \hat{\mathscr{P}} \qquad (34)$$

where, denoting $1-\hat{\mathscr{P}}$ as $\hat{\mathscr{Q}}$,

$$\Omega(z) \equiv \nabla^N \cdot \int d\mathbf{p}^N \frac{\mathbf{p}^N}{m} (z - \hat{\mathscr{Q}}L_N)^{-1} \hat{\mathscr{Q}}\Phi_N(\mathbf{p}^N) \frac{\mathbf{p}^N}{m} \cdot [\nabla^N + \beta(\nabla^N U_N)] \qquad (35)$$

and ∇^N represents the N vectors consisting of N gradient operators $\nabla_1, \nabla_2, \ldots, \nabla_N$, and $U_N(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ is the N-particle potential energy, and β the inverse of the Boltzmann constant times the absolute temperature. Derivation of (34) makes use of the following facts. First, since L_N changes sign under time reversal, we must have $\hat{\mathscr{P}}L_N\hat{\mathscr{P}} = 0$. Second, in disentangling the expression $\hat{\mathscr{P}}L_N(z-\hat{\mathscr{Q}}L_N)^{-1} \hat{\mathscr{Q}}L_N\hat{\mathscr{P}}$, we use, for an arbitrary phase space function $\hat{X}$,

$$L_N\hat{\mathscr{P}}\hat{X} = -\frac{\mathbf{p}^N}{m} \cdot [\nabla^N + \beta(\nabla^N U_N)] \hat{\mathscr{P}}\hat{X}$$

$$\hat{\mathscr{P}}L_N\hat{X} = -\Phi_N(\mathbf{p}^N) \nabla^N \cdot \int d\mathbf{p}'^N \frac{\mathbf{p}'^N}{m} \hat{X}(\mathbf{p}'^N, \mathbf{r}'^N)$$

These results can be readily obtained using the explicit form of L_N. Hence (32) is expressed as

$$C^L(z) = \langle A\mathscr{P}[z-\Omega(z)]^{-1} \mathscr{P}A^* \rangle \qquad (36)$$

where the bra and ket notation are now referred to the N-particle configuration space instead of the phase space. We can then use the general formulation of the preceding section. Note that we cannot do this directly for the third member of (32) since $E(z)$ simply vanishes due to time-reversal symmetry.

The Smoluchowsky model of colloidal suspension without the hydrodynamic interaction readily follows if we replace the expression in (34) sandwiched between ∇^N and $[\nabla^N + \beta(\nabla^N U_N)]$ by $D_0 \mathbf{1}^N$, where D_0 is a constant and $\mathbf{1}^N$ is a unit dyadic in the $3N$-dimensional configuration space. In this case, it is known that D_0 is responsible for both the friction constant acting on a Brownian particle and the random force of thermal origin due to the fluctuation-dissipation theorem.

In our general case, the situation is not clear and here we only make a few remarks. For the values of $|z|$ much smaller than $\omega_0 = k_0/[\beta m S(k_0)]^{1/2}$ with k_0 near the first maximum of $S(k)$, which corresponds to the frequency of the. local oscillation of atoms, we may use the approximation similar to that mentioned above in connection with the Smoluchowsky equation. This long-time behavior was already considered elsewhere.[5, 6] For $|z| \gg \omega_0$ we have

$$E(z) \cong -\omega_0^2/z$$

If $|M^{\mathrm{ir}}(z)/E(z)|$ can be neglected, that is, $|M^{\mathrm{ir}}(z)|$ is much smaller than $\omega_0^2/|z|$, we would have

$$C^L(z) \cong [z + \omega_0^2/z]^{-1}$$

This purely oscillatory behavior might be related to the boson peak.[7-9]

In any case, utility of the present formulation remains to be seen until some ways can be found to deal with $E(z)$ and $M^{\mathrm{ir}}(z)$.

4. CONCLUDING REMARKS

In this paper we have presented an extension of the irreducible memory function approach to the cases other than purely dissipative cases considered before. The work is still in its developing stage and much more remains to be done. Besides the task of finding some useful approximation methods for $E(z)$ and $M^{\mathrm{ir}}(z)$, as in the previous case, we still lack intuitive understanding about the way the operator $\Omega(z)$ is split in order to obtain the irreducible memory function. Nevertheless we hope to see more progress on both aspects in the future.

ACKNOWLEDGMENTS

The author would like to thank W. Götze for informative conversation and correspondence concerning the Boson peak problem.

It is a pleasure to dedicate this article to Mathieu Ernst on the occasion of his 60th birthday. I recall that my interest in the kinetic theory of fluids was triggered by his seminal paper with E. G. D. Cohen concerning the Green–Kubo formulas. I expect Mathieu to remain scientifically active for many more years to come following the example of his mentor.

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