Validity of RPA for the initial state in the time evolution of a fluid

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Abstract
Zwanzig introduced a projection operator $\hat{P}_z$ such that $\hat{P}_z f$, where f solves the Liouville equation, obeys a closed kinetic equation. On multiplying $\hat{P}_z f$ by a finite set of phase functions $\{\hat{A}_i(x)\}$ and integrating over phase space, we get values $\{\alpha_i\}$ agreeing with those calculated from f. Furthermore, one can find $\hat{P}$ such that $\hat{P} f = f_r$ has a specified form, e.g. f_T, the linearization of the Jaynes distribution f_J, and also satisfies the integral conditions imposed on $\hat{P}_z f$. The equation for $f_r = f_T$ given by Los linearizes the Robertson kinetic equation for f_J. Multiplying the Los equation by $\hat{A}_i(x)$ and integrating over x, we get an equation for $\dot{\alpha}_i$ describing the irreversible approach to equilibrium. This agrees with existing phenomenology if the initial state term involving $f_T(0, x)$ vanishes and relaxation times are > 0. Here we show that the initial state term vanishes if $t = 0$ is far enough along in system evolution and $C(t) = \langle \hat{A}\hat{A}(t) \rangle$ decays exponentially at long times. This work addresses problems left hitherto incomplete in the projection operator approach to irreversibility.

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1. Introduction

Following the original work of Zwanzig [1], a number of approaches have used a projection operator $\hat{P}$ to define a 'relevant part' f_r and 'irrelevant part' f_i of the exact solution f of the Liouville equation

$$\dot{f} = -\mathrm{i}\hat{L} f \tag{1}$$

with

$$f_r \equiv \hat{P} f \tag{2a}$$

$$f_i \equiv (1 - \hat{P})f \equiv \hat{Q} f. \tag{2b}$$

$\hat{L}$ is the self-adjoint Liouville operator. f_r gives exactly a set of statistical expectation values

$$\alpha_i \equiv \int f \hat{A}_i(x)\,\mathrm{d}x = \int f_r \hat{A}_i(x)\,\mathrm{d}x \qquad (1 \leqslant i \leqslant \nu) \tag{3}$$

where integration is over the accessible phase space, and $\hat{A}_i(x)$ depends on the phase coordinates x of the system. The values $\{\alpha_i(t)\}$ predict quantities obtainable from the data in a given experiment.

From (1), by operating with $\hat{P}$, one can derive [1, 2] equations for $\dot{f}_r$ and $\dot{f}_i$. Using the second of these equations to eliminate f_i from the first, one gets the closed equation [2]

$$\partial f_r/\partial t = -i\hat{P}\hat{L}f_r - \int_0^t \hat{P}\hat{L}\exp[-\hat{Q}\hat{L}(t-t_1)]\hat{Q}\hat{L}f_r(t_1, x)\,dt_1 - i\hat{P}\hat{L}\exp[-i\hat{Q}\hat{L}t]f_i(0, x) \tag{4}$$

in which we can set $f_i = f - f_r$. Multiplying (4) successively by functions $\{\hat{A}_i(x)\}$ and integrating over x, one obtains evolution equations for the measurable variables $\{\alpha_i(t)\}$ which characterize a non-equilibrium state. Since f_r satisfies (4) whilst (4) is exact, the kinetic equations obtained as moments of (4) are also exact. The evolution equations describe experiment provided the set $\{\alpha_i\}$ includes all variables whose values can be extracted from the data we seek to analyse. The projection operator approach will successfully predict irreversibility from the Liouville equation if we can evaluate moments of all the terms in (4) including the initial state term involving f_i. Calculation of this term has been neglected save by Los [2].

The moment equations for $\dot{\alpha}_i(1 \leqslant i \leqslant \nu)$ obtained from (4) can be cast [1, 3] in the form of phenomenological equations of non-equilibrium thermodynamics, provided we can assume that $t = 0$ is so far in the past that the contribution $[\dot{\alpha}]_0$ to $\dot{\alpha}$ of the initial state term involving $f_i(0, x)$ can be neglected. Here and in what follows we take $\nu = 1$ for computational simplicity and consider the evolution of one variable $\alpha = \int f_r \hat{A}(x)\,dx$. We have

$$[\dot{\alpha}]_0 \equiv -\int \hat{A}i\hat{L}\exp[-i\hat{Q}\hat{L}t]\hat{Q}f(0, x)\,dx$$

$$= (\partial/\partial t)\int \hat{A}\exp[-iL\hat{Q}t]f(0, x)\,dx. \tag{5}$$

When the initial state distribution, $f(0, x)$, which is the $t \to 0$ limit of the solution of (1), is not known, we are led to average over all possible initial states. The random phase approximation (RPA) takes this average to be zero provided $t \gg 0$. If $t \sim 0$, $[\dot{\alpha}]_0$ must be taken into account. Los [2] shows that $[\dot{\alpha}]_0$ will vanish as t increases provided correlations $\langle \hat{A}_i \hat{A}_j \cdots \hat{A}_k(t) \rangle$ of two or more operators vanish with increasing time. Here we shall make a statistical evaluation of (5) showing that it will indeed vanish at times of the order of those considered in the evolution equations of non-equilibrium thermodynamics, e.g. the period of an ultrasonic wave. RPA will be correct if $\alpha(t)$ and $C(t) \equiv \langle \hat{A}\hat{A}(t) \rangle$ have the same relaxation time. That these times are equal follows from the Onsager fluctuation-regression hypothesis used to prove Onsager symmetry in classical irreversible thermodynamics [4]. This hypothesis can be weakened somewhat (cf section 3).

In some cases, one can readily define $\hat{P}$ so that $f_r = \hat{P}f$ has a predetermined form. For example, if $\int f_0 \hat{A}_i(x)\hat{A}_j(x)\,dx = \delta_{ij}$, then for $\chi(x)$ an arbitrary integrable function take

$$\hat{P}\chi \equiv f_0 \sum_{i \geqslant 0} \hat{A}_i(x) \int \hat{A}_i(y)\chi(y)\,dy \tag{6a}$$

$$\hat{A}_0(x) \equiv 1 \tag{6b}$$

$$f_0 = \tilde{V}^{-1}. \tag{6c}$$

Here we assume an energy-shell ensemble with $\tilde{V}$, the volume of the shell over which x-integrations are taken. f_0 is the equilibrium distribution. With this definition one gets

$$\hat{P} f \equiv f_T(t, x) = f_0 \left[1 + \sum_{i=1}^{\nu} \alpha(t) \hat{A}_i(x) \right] \tag{7}$$

where f_T is the linearization of the Jaynesian distribution, $f_J(t, x)$ [5]. f_J is obtained by minimizing the Shannon information [6] and f_T by minimizing the Tsallis information measure I_q[7] for $q = 2$

$$I_2[\tilde{f}] \equiv \int \tilde{f}(x, t)^2 \, \mathrm{d}x. \tag{8}$$

The minimization in both cases, i.e. f_J and f_T, is done subject to conditions (3).

In this paper, the importance of f_T stems from the fact that it yields exact moments α_i, since it obeys (3), and by taking moments of (4) one obtains an exact linear equation which depends parametrically only on the set $\{\alpha_i\}$ at times t long enough such that we can neglect $[\dot{\alpha}]_0$. It follows that if this timescale coincides with the timescale appropriate to the measurements described in non-equilibrium thermodynamics, then the evolution equations will be linear. This linearity does not extend to entropy which is still the functional of f_J given by Shannon [6]. Thermodynamic potentials do not necessarily exhibit the linearity of the evolution equations.

The linearity implicit in (4) when $f_r = f_T$ appears to contradict the work of Robertson [3] who derived a corresponding equation for f_J which also claims to be exact if we can neglect the initial state term. Robertson [3] defines an operator $\hat{P}_R \dot{f} = \dot{f}_J$. Applying P_R to the Liouville equation, one gets an equation for $\dot{f}_J$ which is highly nonlinear.

In [3], the initial state term is eliminated, in accord with RPA, via the boundary condition $f(0, x) = f_J(0, x)$. The corresponding condition in (4) sets $f_i(0, x) = f(0, x) - f_T(0, x) = 0$. As observed by Los [2], f_T is obtained by projecting out the higher correlations. $f_i(0, x) = 0$ provided we take $t = 0$ to be a point in the system evolution where the $\langle \hat{A}_i \hat{A}_j \cdots \hat{A}_k(t) \rangle$ having three or more operators have relaxed. This condition permits us to neglect the nonlinear terms in the Robertson formalism [3]. The relaxation times for the correlations have been estimated [8] to be $\sim 10^{-11}$ s in a simple fluid provided α is a flux of heat or momentum. Accordingly, if one is measuring transport in steady states or at ultrasonic frequencies, we have t large compared with the time for relaxation of the higher correlations. Robertson nonlinearities should not be seen.

With $\nu = 1$ and $\langle \hat{A}(x) \rangle = \alpha$, the linearized Robertson equation for $\alpha(t)$ has the form

$$\dot{\alpha} = -(1/\tau_\alpha)(\alpha - \alpha_0) + [\dot{\alpha}]_0. \tag{9}$$

The first term on the right-hand side comes from taking the moment of the second term on the right-hand side in (4). Although the Zwanzig projection operator approach was developed nearly 40 years ago, it is only recently that a way has been found of showing that $\tau_\alpha > 0$, in agreement with other response theories. The long effort to evaluate τ_α sparked a debate on whether evolution equations derived from (1) can exhibit irreversibility. The original Zwanzig formalism [1] defined $\hat{P}$ in terms of Dirac deltas, yielding a decay constant in (1) whose value was hard to calculate. Here we shall define $\hat{P}$ in (6a) for the linearized Robertson formalism, giving an expression for τ_α in terms of a correlation function which agrees with the fluctuation-dissipation theorem. This agreement has been shown in [10].

The term $[\dot{a}]_0$ has generally been set equal to zero by invoking RPA, with Los [2] the notable exception. The technique developed in [10] for evaluation of τ_α can also be applied to the calculation of $[\dot{a}]_0$. This calculation and the simplified form of the initial state term

based on (4) rather than on the nonlinear Robertson equation for f_J are the principal new contributions of this work. To evaluate $[\dot{a}]_0$, one needs the ω-transform $C(\omega)$ of the correlation $\langle \hat{A} \hat{A}(t) \rangle_0$ in an equilibrium ensemble. According to (9), $\alpha(t)$ decays exponentially at long times. The Onsager fluctuation-regression hypothesis assumes that $\alpha(t)$ and $\hat{A}(x, t)$ decay in the same way, and this has been a basic assumption in non-equilibrium thermodynamics [4] used to derive reciprocity relations. The attention given here to the exponential decay model at long times should not be taken as an assertion that the exponential decay applies to all cases or that exponential decay is necessary to make $[\dot{a}]_0 \to 0$ at long times.

In the following section, an operator identity is used to express the Fourier ω-transform of $[\dot{\alpha}]_0$ as a sum of powers of the ω-transform of $\dot{C}(t)$. These powers constitute a geometric series which can be summed. To invert the transform, one needs its poles which include the zeros of $C(\omega)$ in the lower half ω-plane. These are estimated in section 3 for a model of $C(t)$ described in [11] which can be exact as we please at short times and which decays exponentially as $t \to \infty$. As explained above, this model postulates long-time exponential decay of $\dot{C}(t)$ commonly assumed in non-equilibrium thermodynamics [4]. The estimates in section 4 show that $[\dot{\alpha}]_0$ decays at long times. The final section reviews and summarizes the whole paper.

2. Exact calculation of the initial state term in the evolution equations

To calculate the transform of the initial state term $[\dot{\alpha}]_0$, we expand the integrand in (5) in powers of $i\hat{L}\hat{P}$ using the identity ([3], equation (A1))

$$\exp[(A' + B')s] = \exp(A's) + \int_0^s d\xi [\exp(\xi A')B' \exp[(s - \xi)(A' + B')]] \tag{10}$$

and set

$$A' = -i\hat{L}, \qquad B' = i\hat{L}\hat{P}. \tag{11}$$

Iterating the expression in (10), we obtain

$$\exp[-i\hat{L}\hat{Q}t] = \exp(-i\hat{L}t) + \int_0^t d\xi \exp(-iL\xi)i\hat{L}\hat{P} \exp[-i\hat{L}(t - \xi)]$$

$$+ \int_0^t d\xi [\exp(-iL\xi)i\hat{L}\hat{P} \int_0^{t-\xi} d\xi' \{\exp(-i\hat{L}\xi')\}i\hat{L}\hat{P}$$

$$\times \exp[-(t - \xi - \xi')i\hat{L}] + \cdots . \tag{12}$$

This yields

$$\psi_f(t) \equiv \tilde{V}^{-1} \int \hat{A} \exp[-\hat{L}\hat{Q}t]f(0, x) \, dx \equiv \langle \hat{A} \exp[-\hat{L}\hat{Q}t]f(0, x)\rangle_0$$

$$= \langle A \exp(-iLt)f(0, x)\rangle_0 + \int_0^t d\xi \langle A \exp(-iL\xi)iLA\rangle_0$$

$$\times \langle A \exp[-iL(t - \xi)]f(0, x)\rangle_0 + \cdots . \tag{13}$$

Comparison with (5) shows that $\tilde{V}^{-1}[\dot{\alpha}]_0 = \partial \psi_f(t)/\partial t$.

In order to evaluate $\psi_f(t)$, we calculate the transform $\psi_f(\omega)$ and then invert the latter to obtain an expression which goes to zero at long times. Taking advantage of the convolution

in the products of integrals in (13), we obtain

$$\psi_f(\omega) \equiv \int_0^\infty \psi_f(t) \exp(i\omega t)\,dt = C_f(\omega)[1 - \tilde{C}(\omega) + \tilde{C}^2(\omega) - \cdots]$$
$$= C_f(\omega)/[1 + \tilde{C}(\omega)] \tag{14a}$$

$$C_f(\omega) \equiv \int_0^\infty \langle \hat{A} \exp(-i\hat{L}t) f(0, x)\rangle_0 \exp(i\omega t)\,dt \tag{14b}$$

$$\tilde{C}(\omega) \equiv \int_0^\infty \langle i\hat{L}\hat{A} \exp(-i\hat{L}t)\hat{A}\rangle_0 \exp(i\omega t)\,dt. \tag{14c}$$

The convolution converts the transform of a product into a power of factors $\tilde{C}(\omega)$. The geometric series in (14a) can be summed. Integrating by parts in (14c) and using the result in (14a), we have

$$\tilde{C}(\omega) = -1 - i\omega C(\omega) \tag{15a}$$

$$\psi_f(\omega) = -C_f(\omega)/i\omega C(\omega) \tag{15b}$$

$$\psi_f(t) = (1/2\pi) \int_{-\infty}^\infty \psi_f(\omega) \exp(-i\omega t)\,d\omega. \tag{15c}$$

To evaluate (15c) choose a contour closed in the lower half ω-plane. $\psi_f(\omega)$, from (15b), has a pole at $\omega = 0$. This makes a time-independent contribution to $\psi(t)$ and therefore, from (5), a zero contribution to $[\dot{a}]_0$. $\psi_f(\omega)$ will have additional poles if $C(\omega)$ has zeros in the lower half ω-plane. These contribute exponentially decaying terms to $\psi_f(t)$ and to $\tilde{V}\partial\psi_f/\partial t$. Whether such terms exist or whether RPA holds depends sensitively on the analytical form of $C(t)$. In section 3 we calculate $C(\omega)$ using a realistic ansatz for $C(t)$ designed to give correct results at short and long times [11].

3. Zeros of $C(\omega)$ for a realistic correlation model

In [11], it is pointed out that the velocity autocorrelation function decays at long times as $t^{-d/2}$, and so correlations of conserved variables will not decay exponentially in general as $t \to \infty$. However, variables $\hat{A}(x)$ such as the heat flux, whose values are used as relaxing parameters in non-equilibrium thermodynamics, are non-conserved, and exponential decay is consistent with the Onsager fluctuation-regression hypothesis.

We can also construct an argument stronger and more general than the one based on the Onsager hypothesis. Suppose that t is very long and that we are close to equilibrium, so that a linear equation (9) should be valid. If α is a heat flux component, its equilibrium value $\alpha_0 = 0$ and

$$\alpha = \alpha(0) \exp(-t/\tau_\alpha).$$

We can construct the time correlation

$$\langle \hat{A}(x, 0)\hat{A}(x, t)\rangle_0 = \tilde{V}^{-1} \sum_\alpha \alpha \int \phi(x|\alpha)\hat{A}(x, t)\,dx$$

$$= V^{-1} \sum_\alpha \alpha^2 \exp(-t/\tau_\alpha) = \langle A(x, 0)A(x, 0)\rangle_0 \exp(-t/\tau_\alpha) \tag{16}$$

where we sum over all values α of $\hat{A}(x)$, and $\phi(x|\alpha)$ is the phase space distribution at $t = 0$ given that $\hat{A}(x, 0) = \alpha$. We find that $C(t) = C_\infty(t)$, the exponential form, provided (9)

represents the experimental result at very long times. The latter is given by the statistical average of $\hat{A}(x, t)$ calculated via the distribution function $\phi(x|\alpha)$.

We seek an ansatz for $C(t)$ consistent with the exponential decay of $C(t)$ as $t \to \infty$ and also consistent with a short-time expansion in powers of t^2. We have for small t

$$C(t) = \langle \hat{A} \exp(-i\hat{L}t)\hat{A}\rangle_0 = \sum_{n \geqslant 0} (2n)!^{-1}\langle \hat{A}\hat{L}^{2n}\hat{A}\rangle_0 t^{2n}. \tag{17}$$

$\dot{C}(t) \underset{t \to 0}{\to} 0$ which is not true of the simple exponential,

$$C_\infty(t) \equiv \langle \hat{A}^2\rangle_0 \exp(-\lambda t). \tag{18}$$

Here we normalize $\hat{A}$ so that $\langle \hat{A}^2\rangle_0 = 1$. For long times, it can be shown, invoking the fluctuation-dissipation theorem for τ, that

$$\dot{\alpha} \underset{t \to \infty}{\to} -(1/\tau)(\alpha - \alpha(\infty)) \tag{19a}$$

$$\tau = \int_0^\infty C(t')\,dt'. \tag{19b}$$

Expression (19b) for τ is obtained [10] within a linearized Robertson approximation when an analysis similar to that of the preceding section is applied to the relaxing term in $\dot{\alpha}$. If we use $C_\infty(t)$ for $C(t)$ in (19b), we get $\tau = \lambda$ which is also a consequence of the Onsager fluctuation-regression hypothesis. $C_\infty(t)$ is thus a model for $C(t)$ consistent with non-equilibrium thermodynamics.

A representation $a_0(t)$ for $C(t)$ which interpolates between (17) at $t \to 0$ and $C_\infty(t)$ at $t \to \infty$, keeping a finite but arbitrary number of terms in the t^2 expansion, is [11]

$$a_0(t) = \sum_{p=1}^{P_m} b_p t^{2p-2} \operatorname{sech}(py_1 t) \tag{20a}$$

$$a_0(t) \underset{t \to \infty}{\to} 2b_1 \exp(-y_1 t) \tag{20b}$$

where p_m is the arbitrarily-chosen number of terms. The $\{b_p\}$ can be adjusted to make $a_0(t)$ agree with (17) as $t \to 0$ to the number of terms chosen, whilst y_1 agrees with (18b). Differing numbers p_m of terms characterize different models.

All the models generated by (20a) predict that $a_0(\omega)$ has no zeros in the lower half ω-plane and that, if $a_0(\omega)$ is used as a model for $C(\omega)$, then the poles of $\psi_f(\omega)$ in (14b) must arise from those of $C_f(\omega)$, except for the one at $\omega = 0$. Any simple poles of $\psi_f(\omega)$ will cause an exponential decay of $a_0(t)$ when the ω-transform is inverted unless $C(\omega)$ has a pole at the same ω as does $C_f(\omega)$.

The simplest approximation to (20a) keeps only the $p = 1 = p_m$ term:

$$a_0^1(t) = b_1 \operatorname{sech}(y_1 t). \tag{21}$$

This satisfies $a_0^1(t)_{t \to 0}$ and also (20b). Setting $\beta \equiv py_1$, we expand

$$\operatorname{sech}(\beta t) = 2[e^{-\beta t} - e^{-3\beta t} + e^{-5\beta t} - e^{-7\beta t} + \cdots] \tag{22a}$$

$$a^1(\omega) \equiv \int_0^\infty \exp(i\omega t)a_1^1(t)\,dt$$
$$= -2b_1 \sum_{k \geqslant 1} (-)^k[i\omega - (2k+1)\beta]^{-1}. \tag{22b}$$

We wish to find $\omega = \omega_r + i\omega_i$ such that $a^1(\omega) = 0$. To have a zero of $a^1(\omega)$, we must have $\omega_r = 0$. Then

$$a^1(\omega) \equiv a^1_i(\omega_i) = 2b_1 \sum_{k \geqslant 0} (-)^k [\omega_i + (2k+1)\beta]^{-1}. \tag{23}$$

$a^1_i(\omega_i)$ has poles in the lower half-plane at

$$\omega_i / \beta \equiv \bar{\omega}_i = -(2k+1) \qquad (k = 0, 1, 2, \ldots). \tag{24}$$

Let K be an even integer and > 0 and let $\bar{\omega}_i$ vary over the interval $-(2K+1) < \bar{\omega}_i < -(2K-1)$. The terms $k = K$ and $k = K - 1$ in the sum in (22) are both > 0. Terms with $k > K$ alternate in sign and decrease with magnitude of K and so the sum of any number of terms with $k \geqslant K$ is > 0. Similarly, the sum of terms with $k \leqslant K - 1$ is > 0, and so $a^1_i(\omega_i)$ has no zeros in this interval. If K is odd, we have a similar result, except that the sums are < 0. $a^1(\omega)$ has no zeros in the lower half ω-plane.

Accordingly, using $a^1(\omega)$ as the model for $C(\omega)$ in (15b), we find from (15c) that $\psi(t)$ can derive its time dependence only from poles of $C_f(\omega)$. In (19a), $b_1 = 1$ and sgn $b_p = (-)^{p+1}$. The $\{b\}_p$ with $p > 1$ can be adjusted to fit experiment or a numerical valuation of the expansion coefficients in (17).

Letting $a^p_0(t)$ be the p-term in (20a) for any $p \geqslant 1$, we have

$$a^p(\omega_i) = b_p(-)^m \left(\partial^{2m} / \partial \omega_i^{2m}\right) b_p a^1_p(\omega_i)$$
$$= b_p(-)^m \sum_{k \geqslant 0} (-)^k (2m)! / [\omega_i + (2k+1)\beta]^{2m+1} \qquad (p > 1, m \equiv p - 1). \tag{25}$$

a^p for $p > 1$ has infinities at the same values of ω_i as does $a^1(\omega)$, and the K term in (25) for arbitrary K term in (23), taking into account the sign of b_p. Therefore, the ω-transform of $a_0(t)$ will have no zeros in the lower half ω-plane, however many terms we take in the sum over $p \geqslant 1$. The only pole contributing to the integral in (15c) is the one at $\omega = 0$, and this yields a constant for $\psi(t)$, unless $C_f(\omega)$, where

$$C_f(\omega) = \int_0^\infty \langle Af(t) \rangle_0 \exp(i\omega t)\, \mathrm{d}t = \tilde{V}^{-1} \alpha(\omega), \tag{26}$$

has a pole.

4. Comparison of the exact initial state term with RPA

Let us note at the outset that RPA would cause $\psi_f(\omega)$ to vanish, whereas we want to use RPA to justify setting $\psi_f(t) = \text{constant}$, making $[\dot{\alpha}]_0 = 0$. If that holds, then we say RPA is exact, although $\psi_f(\omega)$ may not vanish. RPA leads to the correct result but does not agree in all respects with the present analysis. We proceed here to show that if t is large enough so that $C(t)$ can be represented by $C_\infty(t)$ in (18), as implied by (20b), then RPA applied to $[\dot{a}]_0$ agrees with the exact result for $\dot{\psi}_f(t)$.

If $\alpha(t)$ relaxes with the relaxation time τ given by the fluctuation-dissipation theorem, then τ is given by (22b). If we use $C_\infty(t)$ as a model for $C(t)$, with λ being the relaxation time of $C_\infty(t)$, then $\tau = \lambda$, and from (25) both $\alpha(\omega)$ and $C_f(\omega)$ have poles at the same point ω [10]. The ratio $\alpha(\omega)/C_f(\omega)$ has no pole at this point. Inversion of the transform $\psi_f(\omega)$ leads to $\psi_f = \text{constant}$, and

$$[\dot{\alpha}]_0 = \dot{\psi}_f(t) = 0. \tag{27}$$

In general, we have from the ω-transform of (4)

$$\dot{\alpha}(\omega) = \int_0^\infty \exp(\mathrm{i}\omega t)\dot{\alpha}(t)\,\mathrm{d}t = -\alpha(0) - \mathrm{i}\omega\alpha(\omega)$$

$$= -\mathrm{i}\omega \int_0^\infty \mathrm{d}t \exp(\mathrm{i}\omega t) \int_0^t \langle \mathrm{i}\hat{L}\hat{A} \exp[-\mathrm{i}\hat{Q}\hat{L}(t - t_1)]\hat{A}\alpha(t_1)\,\mathrm{d}t_1\rangle_0 + [\dot{\alpha}]_0(\omega)$$

$$= -\mathrm{i}\omega\alpha(\omega) \int_0^\infty \mathrm{d}t \exp(\mathrm{i}\omega t)\langle \mathrm{i}\hat{L}\hat{A} \exp[-\mathrm{i}\hat{Q}\hat{L}t]\hat{A}\rangle_0 + [\dot{\alpha}]_0(\omega)$$

$$= -\mathrm{i}\omega\alpha(\omega)\psi(\omega) + [\dot{\alpha}]_0(\omega) = -\mathrm{i}\omega\alpha(\omega)[1 + \tilde{C}(\omega)] + [\dot{\alpha}]_0(\omega) \qquad (28)$$

where

$$\psi(t) \equiv \langle \mathrm{i}\hat{L}\hat{A} \exp[-\mathrm{i}\hat{Q}\hat{L}t]\hat{A}\rangle_0. \qquad (29)$$

$\psi(\omega)$ can be evaluated with the aid of (11) and (12), by analogy with the expansion of $\psi_f(\omega)$. Then equations (28) and (29) can be put [10] in the form

$$\alpha(\omega)[\mathrm{i}\omega + \{(\tilde{C}(\omega) + 1)/C(\omega)\}] = 0. \qquad (30)$$

According to (15a), the square bracket vanishes identically. Therefore, if we do not use RPA and, rather, retain the initial state term in $\dot{\alpha}$, then the equation for $\dot{\alpha}$ extracted from (4) does not determine $\alpha(t)$. To determine $\alpha(t)$ for all times, including very short time, we need the exact solution $f(t)$ of (2) to substitute into (4).

If the time t is $\gg 0$, so that we can apply RPA and set $[\dot{\alpha}]_0 = 0$ in (5) and (28), then calculating $\alpha(\omega)$ from (27), we obtain an expression valid in the time domain of validity of non-equilibrium thermodynamics. Robertson [3] has shown that RPA and (4) give the linear thermodynamic evolution equations. From (29), if $\alpha(\omega)$ is the solution of (28) without the term $[\dot{\alpha}]_0(\omega)$, then substitution of this solution into the initial state term should give an $[\dot{\alpha}](\omega)$ whose inverse transform will vanish. This is illustrated above where the poles in $C_f(\omega)$ and $C(\omega)$ cancel each other, leaving only the pole at $\omega = 0$ in (15b). The latter pole contributes a constant to $C_f(t)$ and zero to $[\dot{\alpha}]_0(t)$. Thus if RPA is used to eliminate the initial state term from the rate equation for $\dot{\alpha}$, the solution of the resulting equation for $\dot{\alpha}$ gives zero when put back into the initial state term. We cannot use non-equilibrium thermodynamics to calculate $\alpha(t)$ for very short times where the initial state term in (4) must be kept. That this should be true is also evident from the circumstances that $\alpha(t)$, V, E are not sufficient as $t \to 0$ to determine the evolution of the system.

5. Summary and conclusion

In the preceding section, it has been shown that if t is large enough and $C(t)$ decays exponentially at long times, we have RPA exact in the sense defined at the beginning of section 4. The relaxation equation (19a) is then obtained which is a phenomenological equation of non-equilibrium thermodynamics. It has been possible to show this without making assumptions about any correlations save the two-operator correlation $C(t)$. If the latter does not decay exponentially, we can still conclude that if $\psi_f(\omega)$ has poles, these will cause $[\dot{\alpha}]_0$ to decay exponentially with time, and if $\psi_f(\omega)$ has no poles, then RPA is exact. That the initial state term in (4) will go to zero as t increases has also been argued by Los [2], and here we present an alternative demonstration based on an exact calculation which invokes the identity (10).

The method used here in calculating $[\dot{a}]_0$ invokes the procedure used in [10] to calculate τ_α in (8). An equation having the form of (9) was derived in [1] to show that evolution equations having the structure of those postulated in non-equilibrium thermodynamics could be obtained

from the Liouville equation (1). However, the Zwanzig projection operators involved Dirac deltas with which it is difficult to calculate, and efforts to prove $\tau_\alpha > 0$ have defied nearly four decades of attempts. This has led to assertions [9] that one cannot extract a prediction of irreversible behaviour from the Liouville equation. The Robertson formalism [3] does not use Dirac deltas, and it recently [10] proved possible to extract τ_α in (9). If α is a component of the heat flux, and we add a driving term proportional to an externally imposed temperature gradient to (9), we can obtain a steady state with $\dot\alpha = 0$ and proportional to τ_α and to the driving term. From (18b), the transport coefficient is proportional to a correlation, as in Kubo–Green theory and as predicted by the fluctuation-dissipation theorem. The result is well known, but how to extract it from the Liouville equation has been a perennial unsolved problem.

The equation for $\dot\alpha$ which results from applying RPA to (4) and using the definition (6a) for $\hat P$ and taking a moment is linear. It is, in fact, the linearization of the corresponding kinetic equation derived by Robertson [3] using his operator $\hat P_R$. The nonlinearities of the Robertson formalism involve [1] correlations $\langle \hat A_i \hat A_j \cdots \hat A_k(t)\rangle_0$ of three or more operators. We can conclude from calculations based on (4) that these higher correlations have relaxed when t is long enough so that $C(t)$ decays exponentially or, more generally, where RPA holds.

We have discussed the equivalence of RPA to the equation $f = \hat P f$. This is analogous to the condition $f = f_J$ postulated by Robertson [3]. It has been observed that $f = \hat P f$ would hold if correlations $\langle \hat A_i \hat A_j(t) \ldots \hat A_k(t')\rangle_0$ and those of higher order had relaxed at t_0, whilst $\langle \hat A \hat A(t)\rangle_0$ is still relaxing. If the relaxation time τ for this correlation is the same as that for α, as prescribed by the Onsager fluctuation-regression hypothesis, the two-particle correlation and α would relax together. Since the time τ is very short when α is the heat flux, we do not observe this relaxation in practice. Extended thermodynamics (EIT) assumes that τ_α does not depend explicitly on time. Thus EIT considers (9) at a time $\gg \tau_\alpha$ at which time the coefficients in (9) are time independent. EIT yields the correct steady-state transport coefficient, but it does not describe accurately the relaxation of the heat flux, which we do not observe. So long as t is long enough, and we are not interested in observing the actual short-time decay of α to its steady-state value, we can suppose that $C(t) = 0$ at t and that all the correlations have relaxed. If we do not want a description of relaxation at time $\sim\tau_\alpha$, we do not have to suppose that the higher-order correlations relax first. It suffices to assume they are all effectively zero at t.

Phenomenological estimates of τ in the case where $\hat A$ is a component of heat or momentum flux give $\tau \sim 10^{-11}$ s [8]. This is much less than the period of an ultrasonic wave or the duration of a steady-state measurement. Therefore, we expect that transport coefficients in simple fluids, at timescales usually used in taking measurements, will be linear. Non-Newtonian viscosities are found e.g. in polymers with transport coefficients dependent on the squares of fluid temperature or velocity gradients. They are also found at very high shear rates [12].

Although the equations for $\dot f_T$ obtained by using the definition (7) in (4) is linear, there still exist possible nonlinearities when the independent variables are particle density and temperature T rather than particle density and energy density which have been used in the above calculations. The Shannon entropy, $-\kappa \,\mathrm{Tr}(f_J \ln f_J)$, where κ is the Boltzmann constant, is still the statistical entropy analogue we need to derive non-equilibrium thermodynamics and the corresponding caloric equation-of-state, agreeing with classical thermodynamics in equilibrium:

$$E = \int f_J \hat H(x)\,\mathrm{d}x. \tag{31}$$

Since f_J is nonlinear, the equation of state and other thermodynamic potentials will, in general, be nonlinear. If this nonlinear equation is used to eliminate E in favour of T in the equation for

$\dot{\alpha}$, the resulting evolution equation will be nonlinear. Specializing the equation to the steady state where $\dot{\alpha} = 0$, we get a nonlinear generalization of Fourier's law with heat conductivity dependent on heat flux or of the Maxwell stress-relaxation equation with relaxation time dependent on the traceless pressure. We cannot say that nonlinearities will not be observed in fluid transport when the temperature and velocity gradients are large enough. Indeed, they are seen [12] in the computer simulations of Couette flow at high shear rates.

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