Exact treatment of initial state term and long-time tails in simplified Robertson formalism

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Abstract

Robertson derived from the Liouville equation an exact equation for a phase function, σ. Taking the product of the σ equation by a phase function $\hat{A}$ and integrating, one gets an exact evolution equation for a variable α defined to be the average of $\hat{A}$ calculated from the Liouville solution. The original Robertson equations were very nonlinear. Contributions from the initial state were neglected. Earlier an equally exact linear version of Robertson equations has been given. An exact solution keeping the initial state has now been found. This solution shows that the time correlation of $\hat{A}$ and $\hat{A}(t)$ is proportional to a solution of the generalized hydrodynamic equations. This solution is much more easily obtained than the correlation itself. We can specify circumstances under which the correlation will decay exponentially or as t to the power of $-d/2$ (d = dimensionality).

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1. Introduction

Robertson [1] devised a projection operator $\hat{P}$ such that $\hat{P}f$, where f solves the Liouville equation, obeys matching conditions:

$$\hat{P}(\partial f/\partial t) = (\partial/\partial t)\sigma(x, t). \tag{1a}$$

$$\alpha(t) = \int f \hat{A}(x) \, dx = \int \sigma \hat{A}(x) \, dx \tag{1b}$$

where x denotes the phase coordinates and σ is an integrable function obeying (1b). We shall assume here that $\hat{P}$ has no explicit time dependence. Integration is over an energy shell $E \leqslant \hat{H}(x) \leqslant E + \Delta E$, where $\hat{H}$ is the Hamiltonian. There are a fixed number N of identical particles. α is a variable which, together with density and temperature, and possible additional variables (not used here), provides a description of the thermodynamic state. Robertson [1] gives a $\hat{P}$ which, operating on the Liouville equation, yields an exact equation for $\partial \sigma / \partial t$. The

latter equation gives an exact moment equation for $\partial\alpha/\partial t$. Robertson's equations were very nonlinear and required approximations, e.g. the random phase approximation RPA. RPA is usually invoked to neglect the dependence of evolution equations on $f(0)$, which Robertson achieves by setting $f(0) = \sigma(0)$. These approximations can be avoided if we use the simplified $\hat{P}$ and σ described in [2].

In [1], $\sigma(x, t)$ was the Jaynesian distribution f_J [3], but the scheme will work so long as the matching condition (1b) is satisfied. This is shown in [2], where it is demonstrated that, if $\hat{A}(x)$ is orthonormal, we can take (for $\chi(x)$ an arbitrary integrable function)

$$\sigma(x, t) = \alpha(t)\hat{A}(x) \qquad (2a)$$

$$\hat{P}(x)\chi \equiv \hat{A}(x) \int dx' \hat{A}(x')\chi(x') \qquad (2b)$$

σ in (2a) does not minimize an information measure and is not a statistical distribution. It is an auxiliary function for which we can obtain an exact equation following the procedures outlined by Robertson. From that equation on multiplying by $\hat{A}(x)$ and integrating over x, we obtain an exact evolution equation for $\alpha(t)$.

If we step-by-step follow the arguments of Robertson [1], and operate with $\hat{P}$ on the Liouville equation (3),

$$\partial f/\partial t = -i\hat{L}f, \qquad (3)$$

where $\hat{L}$ is the self-adjoint Liouville operator, we obtain

$$\partial\sigma/\partial t = -i\hat{P}\hat{L}\sigma(t) + \int_0^t dt' i\hat{P}\hat{L}\hat{T}(t, t')[1 - \hat{P}]i\hat{L}\sigma(t') - i\hat{P}\hat{L}\hat{T}(t, 0)[f(0) - \sigma(0)]. \qquad (4)$$

Here, $T(t, t')$ obeys

$$\partial\hat{T}(t, t')/dt' = i\hat{T}(t, t')(1 - \hat{P})\hat{L}. \qquad (5)$$

When $\hat{P}$ and $\hat{L}$ have no t-dependence,

$$T(t, t') = \exp[(1 - \hat{P})i\hat{L}(t' - t)]. \qquad (6)$$

Equation (4) is exact, and if we multiply (4) by $\hat{A}(x)$ and integrate over x, we obtain the evolution equation for $\partial\alpha/\partial t$. This rate equation can be compared [1] with the phenomenological equations of non-equilibrium thermodynamics if α is a thermodynamic state variable.

Since $\alpha(0)$ does not normally appear in thermodynamic kinetic equations, Robertson [1] set $f(0) = \sigma(0) = f_J(0)$ causing the initial state $(t = 0)$ term to disappear from (4). As remarked above, we can use (2a) instead of f_J for σ, and this will simplify the moment equation for $\dot{\alpha}(t)$ obtained from (4). The simplified equation for $\partial\alpha/\partial t$ is

$$\partial\alpha/\partial t = -\int_0^t dt_1 \int dx\, i\hat{L}\hat{A}\hat{T}(t, t_1)(1 - \hat{P})i\hat{L}A\alpha(t_1) + \int dx\, i\hat{L}\hat{A}\hat{T}(t, 0)[f(0) - \alpha(0)\hat{A}]$$
$$. \qquad (7)$$

In [2], it was observed that the initial state term will vanish if $f = f_J$ at the start and if $t = 0$ is far enough along in the system evolution so that higher correlations have decayed. Here, we find an exact solution for equation (7) with the $t = 0$ term retained. Approximate solutions [4, 5] have been attempted, keeping the initial state term in (4) or in an exact equation for the 'relevant part' of f [4]. However, we are really interested in (7) rather than in (4).

The solution of (7) for $\alpha(t)$ will be obtained in section 2. This asserts that $\alpha(t)$ is proportional to the correlation $C(t) = \langle\hat{A}(x)\exp(-i\hat{L}t)\hat{A}(x)\rangle_0$ where the average is over

an equilibrium ensemble. Accordingly, the long-time behaviour of this and similar time correlations of other variables can be inferred from solution of the generalized hydrodynamic equations obeyed by variables such as $\alpha(t)$. One can obviate the difficult analysis of the asymptotic behaviour of the correlations themselves. The relaxation-rate equation leading to exponential decay for rate processes in a uniform system is given in section 3. In section 4 it is shown that $C(t) \sim t^{-d/2}$ when α obeys a conservation equation in a non-uniform system. In section 5, these results are summarized and discussed. We see that if $\alpha(t)$ is evaluated from the rate equations in sections 3 and 4 then the solution in section 2 immediately gives the asymptotic behaviour of $\langle \hat{A} \hat{A}(t) \rangle_0$ as $t \to \infty$.

2. Solution for $\alpha(t)$

Taking the Fourier transform,

$$\dot{\alpha}(\omega) = \int_0^\infty \exp(\mathrm{i}\omega t)(\partial \alpha/\partial t)\,\mathrm{d}t, \tag{8}$$

we find from (7) that the transform of the initial state term is

$$\psi_0(\omega) = \int_0^\infty \mathrm{d}t \exp(\mathrm{i}\omega t) \int \mathrm{d}x\, \mathrm{i}\hat{L}\hat{A}\hat{T}(t,0)[f(0) - \sigma(0)] = D(\omega)/[1 + \tilde{C}(\omega)] \tag{9a}$$

$$\tilde{C}(\omega) \equiv \int_0^\infty \mathrm{d}t \exp(\mathrm{i}\omega t)C'(t)\,\mathrm{d}t \tag{9b}$$

$$D(\omega) \equiv \int_0^\infty \mathrm{d}t \exp(\mathrm{i}\omega t) \int \mathrm{d}x\, \mathrm{i}\hat{L}\hat{A} \exp[-\mathrm{i}\hat{L}t][f(0) - \sigma(0)]. \tag{9c}$$

To obtain (9a) we use an operator identity to expand $\hat{T}$ in convoluted products of integrals of $\mathrm{i}\hat{P}\hat{L}$. The transform of such a product is a power of $\tilde{C}(\omega)$. $\Psi_0(\omega)$ is proportional to a sum of powers of $\tilde{C}$ which add to give $[1 + \tilde{C}(\omega)]^{-1}$. Details are summarized in [2].

Since the initial state at $t = 0$ does not appear explicitly in the phenomenological equations of non-equilibrium thermodynamics, we would like to impose on $\alpha(t)$ the condition

$$\psi_0(\omega) = 0 = D(\omega). \tag{10}$$

Using the fact that

$$\partial \alpha/\partial t = \int \mathrm{d}x\, \hat{A}\partial f/\partial t$$

$$= \int \mathrm{d}x\, \mathrm{i}\hat{L}\hat{A} \exp(-\mathrm{i}\hat{L}t) f(0) \tag{11}$$

to evaluate the $f(0)$ term in (9c), we find that $D(\omega) = 0$ implies, with $\dot{C}(\omega)$ the transform of $\partial C/\partial t$,

$$\dot{\alpha}(\omega) = \alpha(0)\dot{C}(\omega) \tag{12a}$$

$$\alpha(t) = \alpha(0)C(t). \tag{12b}$$

Provided we have $\alpha(0) \neq 0$ and are describing a process in which $\alpha(t) \to 0$ as $t \to \infty$, (12b) turns out to be an exact solution of (7) when the initial state term is omitted from (7). To see this substitute $\alpha(t) = \alpha(0)C(t)$ for $\alpha(t)$ on the right-hand side of (7) from which the initial state term is omitted. Taking the Fourier transform we have

$$\dot{\alpha}(\omega) = \dot{\alpha}(\omega)[1 + \tilde{C}(\omega)] + \alpha(0) \int_0^\infty \mathrm{d}t \exp(\mathrm{i}\omega t)\mathrm{i}\hat{L}\hat{A}\, \mathrm{e}^{-\mathrm{i}\hat{L}t}\hat{A}\,\mathrm{d}x. \tag{13}$$

Here, we have used (5) to express (7) in terms of $\partial\hat{T}/\partial t_1$ and have integrated over t_1. Equation (13) can be written as

$$\dot{\alpha}(\omega) = [\dot{\alpha}(\omega) + \alpha(0)]\tilde{C}(\omega)/[1 + \tilde{C}(\omega)]. \tag{14}$$

This reduces to (12a).

With the initial state term included (12b), accordingly, is an exact solution of (7). We have not had to assume $t \gg 10^{-9}$ s which was done in [2] to eliminate the initial state term from (4). $\alpha(0)$ in (12b) can be adjusted to fit a measurement made at any time t. We do not have to impose a boundary condition, as did Robertson [1], at $t = 0$.

Whilst (12b) gives us an exact solution for $\alpha(t)$, we must have $C(t)$ in order to use this solution. The correlation is difficult to calculate. A molecular dynamics simulation has shown that the velocity autocorrelation as $t \to \infty$ is $\sim t^{-d/2}$, with d being the system dimensionality [6]. This has led to arguments asserting that most correlations decay as $t^{-d/2}$ including those in Kubo–Green expressions for the transport coefficients.

To elucidate this point, we can use (12b) to predict the $t \to \infty$ behaviour of $C(t)$ from solutions of the generalized hydrodynamic equations satisfied by $\alpha(t)$ and by the velocity $\mathbf{u}(t)$ of mass flow and the energy density, heat flux and pressure. In section 3, we shall discuss the differential equation for $\partial\alpha/\partial t$ and its solution. We can see in which cases the asymptotic solution is exponential, implying from (12b) that the same is true of $C(t)$.

3. Rate equation for α: uniform system

If as $t \to \infty$, $C(t)$ decays exponentially, we can infer from (12b) that $\alpha(t)$ also decays exponentially and that $\alpha(t)$ obeys the rate equation

$$\partial\alpha/\partial t = -(1/\tau)(\alpha - \alpha_0). \tag{15}$$

For processes considered here, $\alpha_0 = 0$. However, molecular dynamics simulations [6] showing that the velocity autocorrelation is proportional to $t^{-d/2}$ have raised objections to a putative exponential behaviour of $C(t)$. Therefore, we must derive (15) from the formalism of section 2 and investigate the circumstances leading to exponential decay.

Equation (12b) implies that

$$\dot{\alpha}(\omega)/\alpha(\omega) = \tilde{C}(\omega)/C(\omega) = [-1/C(\omega))] - i\omega. \tag{16}$$

If $\alpha(t)$ does not decay exponentially, then $\alpha(\omega)$ will have no poles in the lower half ω-plane. If $C(\omega)$ has zeros in the lower half-plane, then

$$\partial\alpha(t)/\partial t = (1/2\pi) \int_{-\infty}^{\infty} \exp(-i\omega t)(\tilde{C}(\omega)/C(\omega))\alpha(\omega)\,d\omega \tag{17}$$

will decay exponentially. To establish this, one chooses a contour closed in the lower half-plane. $\partial\alpha/\partial t$ will not necessarily vanish if the system is non-uniform and the equation for $\partial\alpha/\partial t$ has spatial derivatives, otherwise $\partial\alpha(t)/\partial t = 0$. If $\alpha(t)$ describes a dissipative dynamical process, it will decay exponentially to zero, and (15) will apply in the long-time limit close to equilibrium where the equations are linear.

If α behaves exponentially, (12b) asserts that this is true of the correlation $C(t)$. In section 4, we consider how a $t^{-d/2}$ behaviour can arise. When $\alpha(\mathbf{r}, t)$ can depend on position $\mathbf{r}$, there can be diffusive flows. Conservation laws applicable to such flows, which have not been relevant up to this point, can explain non-exponential decay.

4. Asymptotic behaviour of conserved variables

The variable $\alpha(t)$ considered in section 3 is associated, e.g., with liquid structure. We can divide the volume of the system into regions each with diameter twice the mean separation of two molecules. α can then be the fraction of regions in which local fluctuations in density will permit a molecule to slip past its neighbours. Such an α will relax according to (15) with τ the lifetime of a local expansion. The variable α is associated with a molecular relaxation process contributing [7] to bulk viscosity and energy dissipation.

By contrast, consider the mass velocity **u**

$$m(\mathbf{r}, t)u(\mathbf{r}, t) = \int \sum_{j=1}^{n} (\mathbf{p}_j/m)\delta(\mathbf{r}_i - \mathbf{r})f(t, x)\,\mathrm{d}x \tag{18}$$

at **r** where n is the particle number and m the mass of particle i with momentum $\mathbf{p}_i \cdot \mathbf{u}(\mathbf{r}, t)$ obeys the hydrodynamic equation of momentum conservation. This is obtained not from (4) but from multiplying (3) by the operator $\hat{\mathbf{u}}(\mathbf{r}, x)$ which multiplies f in the integrand of (18) and integrating over x. The analysis of section 2 still applies and we have

$$u(\mathbf{r}, t) = u(\mathbf{r}, 0)C_{\mathrm{vel}}(\mathbf{r}, t) \tag{19}$$

with C_{vel} proportional to the velocity autocorrelation at **r**. The $t \to \infty$ limit of C_{vel} is given by (19) provided we obtain the corresponding limit for $\mathbf{u}(\mathbf{r}, t)$ by solving the hydrodynamic equations.

Suppose that $\alpha(\mathbf{r}, t)$ obeys

$$\partial\alpha(\mathbf{r}, t)/\partial t = \lambda\nabla^2\alpha(\mathbf{r}, t) \tag{20}$$

where λ is proportional, as the case may be, to viscosity or thermal conductivity. We have

$$\alpha(\mathbf{k}, t) \equiv \int \alpha(\mathbf{r}, t)\exp(\mathrm{i}\mathbf{k} \cdot \mathbf{r})\mathrm{d}\mathbf{r} \tag{21a}$$

$$\partial\alpha(\mathbf{k}, t)/\partial t = -\mathbf{k}^2\lambda\alpha(\mathbf{k}, t) \tag{21b}$$

$$\alpha(\mathbf{k}, t) = \alpha(\mathbf{k})\exp(-k^2\lambda t). \tag{21c}$$

Defining $\mathbf{k}' \equiv t^{1/2}k$, we have

$$\alpha(\mathbf{r}, t) = V(2\pi)^{-3}\int \mathrm{d}\mathbf{k}'\alpha_0(\mathbf{k}'t^{-1/2})t^{-d/2}\exp(-\lambda k'^2)\exp(-\mathrm{i}\mathbf{k}' \cdot \mathbf{r}t^{-1/2}). \tag{22}$$

As $t \to \infty$, α_0 is constant save for very large k' which makes a small contribution to the integral. The correlation $\langle\hat{A}(\mathbf{r}, x)\exp(-\mathrm{i}\hat{L}t)\hat{A}(\mathbf{r}, x)\rangle_0$ should be $\sim t^{-d/2}$ as $t \to \infty$.

5. Summary and discussion

In order to eliminate the initial state terms which do not appear in thermodynamic kinetic equations, Robertson [1] assumed $f(0) = \sigma(0)$ in (4). He took $\sigma(x, t) = f_J$, the Jaynesian distribution, which is highly nonlinear. In [2], it is pointed out that if $f = f_J$ at some time and $t = 0$ is a later time, then decay of higher order correlations can make $f(0) - \sigma(0)$ a constant with σ the linear function given by (2a). Under these conditions the initial state term vanishes. Here, we use the linear $\sigma(x, t)$ (2a) which also gives an exact moment equation for $\alpha(t)$, but we make no assumption about vanishing of the $t = 0$ term in (4). Instead we find that the exact solution (12b) makes the initial state term zero in (7). This solution (12b) has an adjustable parameter $\alpha(0)$ which can be determined to fit a measurement at $t = 0$ or at any other time.

Memory of the state at $t = 0$ is not lost. Loss of memory was invoked in the past to justify applying RPA to the $t = 0$ term in (4).

The solution (12b) is of particular interest because it asserts that the asymptotic time dependence of $C(t)$ is the same as that of $\alpha(t)$. Very lengthy calculations have been made [8, 9] of $C(t)$ which show it decays as $t^{-d/2}$ provided the time dependence of $\alpha(t)$ comes from its relation to a variable obeying a conservation equation. A simple demonstration of this is given in section 4. The simplicity of the present result recommends it in comparison with the 15 journal pages used to analyse $C(t)$ [8].

Provided α is a thermodynamic state variable describing a dynamic dissipative rate process then $\alpha(t)$ and $C(t)$ should decay exponentially as $t \to \infty$. To see this observe that if the entropy $S = S(N, T, \alpha)$, the classical thermodynamic rate equation is [10]

$$\dot{\alpha} = -\Lambda \partial F / \partial \alpha \quad (\Lambda > 0) \tag{23}$$

where F is the Helmholtz free energy. At long times, α is close to equilibrium, and (23), when linearized, reduces to (15). Under these circumstances α decays exponentially, as does $C(t)$.

It must be noted that, to achieve Galilean invariance in thermodynamic kinetic equations, such as (15), thermodynamic variables are defined in a frame moving relative to the lab with velocity $\mathbf{u}(r, t)$. This definition is the same for all observers in all inertial frames. The heat flux $\mathbf{J}_Q$ and traceless pressure are defined as energy and momentum flows, respectively, observed in such a frame. These are the fluxes appearing in Kubo–Green expressions for viscosity and thermal conductivity. The energy flux $\mathbf{J}_e$ in the lab frame will differ from $\mathbf{J}_Q$ by a term proportional to $\mathbf{u}$. Therefore $\mathbf{J}_e$ and its time correlation should decay as $t^{-d/2}$. $\mathbf{J}_Q$ and the traceless pressure obey equation (15) known [11,12] as the Cattaneo–Vernotte equation in the case of $\mathbf{J}_Q$ and as the Maxwell stress-relaxation equation [13] in the case of pressure. The corresponding correlations, e.g. $\langle \hat{J}_Q^\alpha \cdot \hat{J}_Q^\alpha(t) \rangle$, should decay exponentially as $t \to \infty$.

Since the solution obtained here is not limited to long times, unlike the case discussed in [2], we can use (12b) to generalize (7) to frequencies higher than ultrasonic if we have a suitable model for $C(t)$. If we can show, using arguments given above, that $C(t)$ is exponential at long times, then we can use existing expressions [14], which interpolate between long-time and short-time behaviour, to extend (7) to shorter times.

Should we desire to extend (7) to somewhat shorter times, but not much shorter, we can try the model

$$C(t) = \text{sech}(at). \tag{24}$$

This simplifies the model of [14] to the case where there is just one constant a rather than a sum of such terms. Using (23) in (12b) and keeping $O[(\exp(-3at)]$, we have

$$\alpha(t) = 2[\exp(-at) - \exp(-3at)] + O[(\exp(-5at)] \tag{25}$$

Equation (7) is generalized to

$$\ddot{\alpha} = -3a^2\alpha - 4a\dot{\alpha}. \tag{26}$$

This is a second-order equation such as we find [10] in extended non-equilibrium thermodynamics. If $\alpha \sim \tau^{-1}$ and τ is the lifetime of a locally expanded region, (26) will apply to frequencies above those of ultrasonic experiments.

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