# A new model to replace simple exponential decay in dynamical time correlations



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# A new model to replace simple exponential decay in dynamical time correlations

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**Abstract.** An ansatz is proposed for the time correlation $C(t) = \langle \hat{F} \exp(-\mathrm{i}\hat{L}t)\hat{F}\rangle_0$ of a non-conserved phase function $\hat{F}$, where $\hat{L}$ is the Liouville operator and the brackets denote an equilibrium canonical average. The new expression decays exponentially as $t \to \infty$ and reduces to a series in powers of $t^2$ as $t \to 0$, agreeing with a finite, arbitrarily chosen, number of terms in an exact $t$-expansion. The ansatz takes the form of a series shown to converge absolutely and uniformly. Its time integral can be fitted to experiment or to a computer simulation by adjusting the decay constant characterizing the long-time behaviour. If the decay constant is sufficiently large, the new model yields results of an order of magnitude consistent with the often-used exponential decay model.

## 1. Introduction

The system to be considered here is a monatomic fluid of $N$ point particles described by a Hamiltonian $\hat{H}(x)$ dependent on the phase coordinates $x$. If $\hat{F}(x)$ is a continuous integrable and differentiable function odd under inversion in momentum space and even under configuration inversion, we are concerned with the equilibrium time correlation ($\hat{L}$ is the Liouville operator),

$$C(t) \equiv Z^{-1} \int \exp(-\beta\hat{H})\hat{F}(x)\,\mathrm{e}^{-\mathrm{i}\hat{L}t}\,\hat{F}(x)\,\mathrm{d}x \equiv \langle \hat{F}\mathrm{e}^{-\mathrm{i}\hat{L}t}\,\hat{F}\rangle_0 \tag{1}$$

with $\beta \equiv 1/\kappa T$, where $\kappa$ is the Boltzmann constant and $Z$ is the canonical partition function. The subscript zero will, in what follows, denote an equilibrium canonical average. If $\hat{F}(x)$ is the heat or diffusion flux, which have the parity we are postulating under inversion, the thermal conductivity [1] or diffusion coefficient [2–4], respectively, are proportional to the time integral of $C(t)$.

To integrate $C(t)$ over an infinite time interval, one usually uses an analytical model which can be fitted to available information from experiment or molecular dynamics. The simplest model proposed [5] is a decaying exponential. Efforts [6, 7] to fit such an exponential to the velocity autocorrelation are contradicted by molecular dynamics [8], which reveals a long-time tail falling off as $t^{-d/2}$ as $t \to \infty$, where $d$ is the system dimensionality. Thus if $C(t)$ is to decay exponentially at long times, we should take $\hat{F}$ to be non-conserved. This property applies in the case of heat and diffusion flows and will be assumed in what follows.

A primary reason for taking $C(t)$ to be exponential at long times stems from the successful use of such a model in non-equilibrium thermodynamics. Define

$$\langle \hat{F}\rangle \equiv \int \rho(t)\,\hat{F}\,\mathrm{d}x \tag{2}$$

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where $\rho$ is the solution of the Liouville equation. A formalism of Robertson [9] has been used [10, 11] to derive from the Liouville equation an evolution equation which, in the linear approximation, is

$$\partial\langle\hat{F}\rangle/\partial t = -(1/\tau)\langle\hat{F}\rangle \tag{3a}$$

$$\tau = \int_0^\infty C(t)\,\mathrm{d}t/\langle\hat{F}^2\rangle_0. \tag{3b}$$

Equation (3*a*) is exact if $\langle\hat{F}\rangle$, $N$ and $T$ are the only quantities for which we extract measured information in an experiment to be analysed. Equation (3*b*) is consistent in the case of heat flow with the fluctuation–dissipation theorem [11, 12]. If a driving force is added to the right-hand member of (3*a*), then in a steady state $\langle\hat{F}\rangle$ will be proportional to this force with a transport coefficient proportional to $\tau$ and thus to the integral of $C(t)$.

Equation (3*b*) will be satisfied if

$$C(t) = \langle\hat{F}\rangle_0\exp(-t/\tau). \tag{4}$$

This is the Onsager fluctuation–regression hypothesis, which postulates that a spontaneous fluctuation in $\hat{F}$ will decay with the same relaxation time as $\langle\hat{F}\rangle$. This hypothesis has been invoked [13] to derive the Onsager reciprocity relations of classical non-equilibrium thermodynamics. Onsager symmetry has been found [10] in linear *extended* thermodynamics which [14] includes variables such as $\langle\hat{F}\rangle$, which are dissipative fluxes in the classical formalism. This statistical result is consistent with supposing that the fluctuation–regression hypothesis is valid in the linear extended domain,

If (4) is valid at timescales of classical non-equilibrium thermodynamics, e.g. in the domain of ultrasonic frequencies ($\omega \lesssim 1$ MHz), it certainly does not hold as $t \to 0$. Expanding (1) in powers of $t$, we find, after $n$ partial integrations in the term $\mathrm{O}(t^{2n})$:

$$a_0(t) \equiv \nu C(t) = \sum_{n\geqslant 0}(1/2n!)(-)^n\tilde{c}_n t^{2n} \tag{5a}$$

$$\nu = (\langle\hat{F}^2\rangle_0)^{-1} \tag{5b}$$

$$\tilde{c}_n \equiv \nu\langle\{(\mathrm{i}\hat{L})^n\hat{F}\}^2\rangle_0 \qquad \tilde{c}_0 = 1. \tag{5c}$$

We shall assume in what follows that the expansion (5*a*) converges over a finite interval $0 \leqslant t \leqslant t_a$. There is no *a priori* reason to suppose $t_a < \infty$, but convergence over an infinite time interval is not necessary. From (1), we see that

$$\partial C(t)/\partial t \underset{t\to 0}{\to} -\langle\hat{F}\mathrm{i}\hat{L}\hat{F}\rangle_0 = 0 \tag{6}$$

which vanishes from the inversion symmetry of $\hat{F}$. Equations (5*a*) and (6) are consistent if (5*a*) can be differentiated term by term. However, equations (5*a*) and (6) are not consistent with the Maclaurin expansion of (4).

The statistical derivation [10] of (3*b*) shows that $\tau$ is time dependent as $t \to 0$. The usual formulation of extended thermodynamics, in which the coefficients have no explicit time dependence, is recovered [15] only for $t \to \infty$. In a formalism which seeks to improve on (4), we need an ansatz which agrees with (5*a*) as $t \to 0$ and which is approximately exponential at long times where the exponential model has worked well in the linear phenomenology.

In the following section we shall introduce a scheme proposed by Lee [16], whereby the sum in (5*a*) is replaced by an approximation which agrees with the exact series (5*a*) to an arbitrary finite number of terms. $\{\tilde{c}_k\}$ in the exact series may be imagined to be found by molecular dynamics. In section 3, we propose an ansatz which agrees with the approximate

Lee model developed in section 2 for $a_0(t)$ at short times and which decays exponentially as $t \to \infty$. The exponent $y_1$ at long times can be determined, as shown in section 4, so that (3*b*) holds when the ansatz of section 3 is introduced under the integral sign, with $\tau$ determined from experiment or computer simulation. It is found in section 4 that, if the computer value of $\tau$ is not too long, there exists a value of $y_1$ consistent with $\tau \sim y_1^{-1}$, so that the model of section 3 can give, to a good approximation, the same value of $\tau$ as does (4). In section 5 we discuss the role of the model of section 3 in bridging the short- and long-time behaviour of $C(t)$. Higher terms in the ansatz for $C(t)$ describe the transition from short-time behaviour of (5*a*) to long-time exponential decay. In practice, the time domain of this transition is so short that we do not actually observe the cross-over. Furthermore, the memory of short-lived correlations may be lost in the transition region. If that happens, an ansatz exact in this region would not reproduce the observations if the relevant measurements could be made.

## 2. Lee model and arguments against exponential behaviour

The Lee approach [16, 17] defines an orthogonal basis set $\{f_j(x)\}$, which spans the Hilbert space of

$$F(t) \equiv \exp(-\mathrm{i}\hat{L}t)\hat{F} = \sum_{j\geqslant 0} a_j(t)\, f_j. \tag{7}$$

$\{a_j(t)\}$ and $\{f_j(t)\}$ satisfy the recurrence relations [16, 17]

$$\Delta_{j+1}a_{j+1} = -\dot{a}_j(t) + a_{j-1}(t) \qquad (j \geqslant 0) \tag{8a}$$

$$\Delta_j \equiv \langle f_j^2\rangle_0/\langle f_{j-1}^2\rangle_0 \qquad (j > 0) \tag{8b}$$

$$f_{j+1} = \mathrm{i}\hat{L}f_j + \Delta_j f_{j-1} \qquad f_{-1} = 0 \qquad f_0 = \hat{F}. \tag{8c}$$

$\{\Delta_j\}$ are the constants in a continued fraction representation of $a_0(\omega) = \nu C(\omega)$, where $a_0(\omega)$ is the Fourier $\omega$-transform of $a_0(t)$. The coefficients (cf equation (5*a*))

$$c_n \equiv \{1/(2n)!\}(-)^n\tilde{c}_n \qquad (n \geqslant 0) \tag{9a}$$

$$c_0 = 1 \tag{9b}$$

can be expressed in terms of $\{\Delta_n\}$. Thus [16]

$$c_1 = -\tfrac{1}{2}\Delta_1 \tag{10a}$$

$$c_2 = (1/4!)\Delta_1(\Delta_1 + \Delta_2) \tag{10b}$$

$$c_3 = -(1/6!)\Delta_1\{(\Delta_1 + \Delta_2)^2 + \Delta_2\Delta_3\} \tag{10c}$$

$$c_4 = (1/8!)\Delta_1\{(\Delta_1 + \Delta_2)^3 + \Delta_2\Delta_3(\Delta_1 + \Delta_2) + \Delta_2\Delta_3(\Delta_1 + \Delta_2 + \Delta_3 + \Delta_4)\}. \tag{10d}$$

Each $c_n$ depends on $\Delta_j$ for $1 \leqslant j \leqslant n$. If the first $a - 1$ $c_j$-coefficients are determined accurately by computer simulation, then the first $a - 1$ $\Delta_j$ are also calculable from (10*a*)–(10*d*) and subsequent equations in this set. If we set $f_{n+1} = 0 = \Delta_{n+1}$ in (8*c*), all $f_j$ and $\Delta_j$ for $j > n$ are zero. Then equations (8*c*) yield an equation for $f_0$ for the solution of which the $n$ values of $\Delta_1, \ldots, \Delta_n$ are boundary conditions. $f_0$ no longer equals $\hat{F}$. This procedure yields an approximation to (5*a*) in which the first $n + 1$ terms are exact, with the rest being calculated from (10*a*)–(10*d*) plus additional equations representing an extension of this set in which $\Delta_p = 0$ for $p > n$. The first $n + 1$ terms are exact, and so $\nu C(t)$ is accurate as $t \to 0$. In the ansatz of section 3, $\nu C(t)$ to $\mathrm{O}(t^2)$ as $t \to 0$ and as $t \to \infty$ is determined by $\Delta_1$ and $\Delta_2$ plus the exponent $y_1$ characterizing decay at very long times. Since it is for long times and low (∼1 MHz) frequencies that we usually make measurements, an approximate theory in which a finite number of $\{\Delta_j\}$ are accurate and the rest zero should fit our observations.

*2.1. Proof that $C(t)$ is not exactly exponential*

Referring to (7) for the definition of $F(t)$, we have [16]

$$\langle F(t)\, F(t)\rangle_0 = \langle \hat{F}^2\rangle_0 \tag{11}$$

since $\langle e^{-i\hat{L}t}\hat{F}e^{-i\hat{L}t}\hat{F}\rangle_0 = \langle \hat{F}e^{i\hat{L}t}e^{-i\hat{L}t}\hat{F}\rangle_0$. To see this, expand $\exp(-i\hat{L}t)\hat{F}$ inside the angular brackets in powers of $t$ and integrate by parts. If $a_0(t) = \nu C(t) = \exp(-\gamma t)$, then (8*a*) implies $a_j = u_j \exp(-\gamma t)$ for all $j \geqslant 1$. Then from (7) $F(t)$ decays as $\exp(-\gamma t)$, which is incompatible with (11). Therefore [16], $C(t)$ cannot be exactly exponential at any $t$ unless external fields have intervened at earlier times to modify the dynamics. Thus the model of section 3, as we shall see, may become effectively an exponential, to a high degree of accuracy, as $t \to \infty$ only if memory of short-lived correlations is lost in the long-time limit.

*2.2. Lee model with finite basis set*

We have stated that, for a suitably chosen $f_0$, all the basis functions $f_j$ for $j > n$, where $n$ is an arbitrarily chosen integer $\geqslant 1$, can be made to vanish. To show explicitly how this is done, set $j + 1 = p$ in (8*c*) and use equations (8*c*) successively to yield

$$f_p = i\hat{L}f_{p-1} + \Delta_{p-1}f_{p-2} = (i\hat{L})^2 f_{p-2} + (\Delta_{p-1} + \Delta_{p-2})i\hat{L}f_{p-3} + \Delta_{p-1}\Delta_{p-3}f_{p-4}. \tag{12}$$

This process can be iterated until the right-hand member involves only $f_0$ and its derivatives. Thus,

$$f_1 = i\hat{L}f_0 \tag{13a}$$

$$f_2 = (i\hat{L})^2 f_0 + \Delta_1 f_0 \tag{13b}$$

$$f_3 = (i\hat{L})^3 f_0 + (\Delta_1 + \Delta_2)i\hat{L}f_0 \tag{13c}$$

$$f_4 = (i\hat{L})^4 f_0 + (\Delta_1 + \Delta_2 + \Delta_3)(i\hat{L})^2 f_0 + \Delta_1\Delta_3 f_0 \tag{13d}$$

$$f_5 = (i\hat{L})^5 f_0 + (\Delta_1 + \Delta_2 + \Delta_3 + \Delta_4)(i\hat{L})^3 f_0 + i\hat{L}f_0\{\Delta_1\Delta_3 + \Delta_4(\Delta_1 + \Delta_2)\}. \tag{13e}$$

Similar equations, expressing $f_n$ in terms of $f_0$ and its derivatives, can be derived for arbitrary positive $n$. Equating to zero the expression for $f_{n+1}$, we obtain an equation for $f_0$ which, according to (8*c*), is consistent with $f_{n+p} = 0 = \Delta_{n+p}$ (all positive integers $p$). We shall suppose that $f_0$ can be determined as the solution for the equation $f_{n+1} = 0$, subject to boundary conditions specifying the values of $\Delta_1, \ldots, \Delta_n$. These values are calculated from exact, computer-generated values of $c_1, \ldots, c_n$. The calculation uses (10*a*)–(10*d*) and additional equations which may be added to that set. The exact values are calculated for the time correlation of $\hat{F}$, although $f_0$, calculated from the result of setting $f_{n+1} = 0$, no longer equals $\hat{F}$. We have, however, a model for the time correlation of $\hat{F}$ which should be valid at short and long times. If the equation for $f_0$ cannot be solved subject to the specified boundary conditions, we still have a model, but it is *ad hoc* and does not fit into the scheme of Lee.

*2.3. Convergence condition derived from a truncated Lee model*

For illustrative purposes, we shall suppose that $f_0$ is the solution of the equation obtained by setting $f_5 = 0$ in (13*e*). The latter equation is presumed to have a solution such that $\Delta_1, \ldots, \Delta_4$ are non-vanishing and agree with exact values calculated from (10*a*)–(10*d*), with the $c_j$ being computer values for the $t$ expansion of $C(t)$ for the function $\hat{F}$ whose time correlation we seek to approximate. The remaining $c$s in (5*a*) are replaced by values calculated from the truncated model. To prove that, after this replacement the modified expansion (5*a*) converges, we need an inequality satisfied by the $\{c_n^*\}$ in (5*a*), where the asterisk denotes values calculated from the truncated model.

Since the truncation model is set up to make $f_{4+p} = 0 = \Delta_{4+p}$ for all positive integers $p$, we obtain by successive applications of (8*c*):

$$0 = f_{4+p} = (\mathrm{i}\hat{L}) f_{4+p-1} + \Delta_{4+p-1} f_{4+p-2}$$
$$= (\mathrm{i}\hat{L})^2 f_{4+p-2} + \Delta_{4+p-2} f_{4+p-3} = (\mathrm{i}\hat{L})^p f_4 + \Delta_4 f_3 \qquad (p > 1). \qquad (14)$$

Multiplying (14) by $f_0$, integrating over phase space, and substituting for $f_4$ from (13*d*), we obtain

$$0 = \langle f_0 (\mathrm{i}\hat{L})^p f_4 \rangle_0 = \langle f_0 (\mathrm{i}\hat{L})^{p+4} f_0 \rangle_0 + \langle f_0 (\Delta_1 + \Delta_2 + \Delta_3)(\mathrm{i}\hat{L})^{p+2} f_0 \rangle_0$$
$$+ \Delta_1 \Delta_3 \langle f_0 (\mathrm{i}\hat{L})^p f_0 \rangle_0. \qquad (15)$$

Here we have used the orthogonality of $\{f_j\}$, i.e. $\langle f_p f_r \rangle_0 = 0$ if $r \neq p$ [16].

Now put $p = 2r$, for $r$ an integer $\geqslant 1$, in (15) and integrate partially. We have

$$\langle f_0 (\mathrm{i}\hat{L})^{2r} f_0 \rangle_0 = (-)^r \langle \{(\mathrm{i}\hat{L})^r f_0\}^2 \rangle_0 = (-)^r \tilde{c}_r^*. \qquad (16)$$

Treating in a similar fashion all three terms in (15), we obtain

$$\tilde{c}_{r+2}^* = (\Delta_1 + \Delta_2 + \Delta_3) \tilde{c}_{r+1}^* - \Delta_1 \Delta_3 \tilde{c}_r^* \qquad (r \geqslant 1). \qquad (17)$$

Taking into account (10*a*) and (10*b*), which assert that $\tilde{c}_0 = 1 = \tilde{c}^*$ and that $\tilde{c}_2 = \Delta_1(\Delta_1 + \Delta_2) = \tilde{c}_2^*$, we have

$$\tilde{c}_{j+1}^* \leqslant (\Delta_1 + \Delta_2 + \Delta_3) \tilde{c}_j^* \qquad (j \geqslant 0). \qquad (18)$$

If, as supposed above, $a = 4$ is the largest $p$ such that $\Delta_p \neq 0$ and $\bar{\Delta} = \max(\Delta_1, \Delta_2, \Delta_3)$, we have from (18) (cf equation (9*a*))

$$\tilde{c}_{j+1}^* \leqslant (a-1)\bar{\Delta} \tilde{c}_j^* \qquad (j \geqslant 0) \qquad (19a)$$

$$|c_{j+1}^*| \equiv [\{2(j+1)\}]^{-1} |\tilde{c}_{j+1}^*| < \{(a-1)\bar{\Delta}/(j+1)\} |c_j^*|. \qquad (19b)$$

From (19*b*) it follows that, for arbitrary, real, positive $y_1$ and $\mathrm{int}(z)$, the smallest integer $\geqslant z$:

$$|c_{j+1}^*| < y_1^2 |c_j^*| \qquad \text{if} \quad j + 1 \geqslant \mathrm{int}\{(a-1)\bar{\Delta}/y_1^2\} \equiv \bar{j} + 1. \qquad (20)$$

Equation (20) is the fundamental inequality needed to prove convergence in (5*a*) when the truncation model is used to calculate the $\{c_n\}$ in that equation, i.e. after replacement of $\tilde{c}_n$ by $\tilde{c}_n^*$. Denoting by $a_0^*$ the result of replacing $\tilde{c}_n$ by $\tilde{c}_n^*$ in (5*a*), we have

$$a_0^* \leqslant S_{\bar{j}} + \sum_{n \geqslant j} |c_n^*| (y_1 t)^{2n} \leqslant S_{\bar{j}} + |c_j^*| (y_1 t)^{2\bar{j}} \{1 - (y_1 t)^2\}^{-1} \qquad (y_1 t < 1) \qquad (21)$$

where $S_{\bar{j}}$ is the sum of the first $\bar{j}$ terms in $a_0^*(t)$. Equation (21) shows that, when the truncation model is used to calculate $\{\tilde{c}_n\}$, equation (5*a*) converges absolutely as $t \to 0$, i.e. for $t < y_1^{-1}$. In section 3, we shall let $y_1$ be the exponential decay constant of $C(t)$ as $t \to \infty$ and show that (20) can be used to prove convergence of the ansatz introduced there and of its time integral. The parameters of the ansatz are evaluated to make it agree with $a_0^*(t)$ as $t \to 0$ and to make it consistent with (3*b*) when $\tau$ is determined independently, e.g. by computer simulation.

## 3. New ansatz fitted to the truncated Lee model and to long-time exponential decay

As indicated in the previous section, we seek to replace (4) with an ansatz which agrees exactly with terms out to $n = 4$ in (5$a$) as $t \to 0$, with the $\{\tilde{c}_j\}$ replaced by $\{\tilde{c}_j^*\}$ calculated from the truncated Lee model in which $f_5 = 0$. These $\{\tilde{c}_j^*\}$ obey (14)–(18) and satisfy the inequalities (19$a$) and (20). Inequality (20) can be used to prove convergence of the sum:

$$a_0^b(t) = \sum_{p=1}^{\infty} b_p t^{2p-2} \operatorname{sech}(py_1 t) \tag{22}$$

where the $\{b_p\}$ are determined to make the Maclaurin expansion of (22) agree identically with $a_0^*(t)$. Equation (22) defines the new model which is exact as $t \to 0$, since the first five terms of $a_0^*$ are exact, whilst the model decays exponentially at long times. The superscript $b$ denotes an approximation to $a_0(t) = \nu C(t)$.

As $t \to \infty$ (22) gives

$$a_0(t) \underset{t\to\infty}{\to} 2b_1 \exp(-y_1 t). \tag{23}$$

To determine $y_1$, we substitute (22) into (3$b$) and adjust $y_1$ so that (3$b$) fits a $\tau$ obtained from molecular dynamics or from experiment. For this it is necessary to prove convergence of the infinite time integral of (22) which is done in section 4. If $y_1 \sim \tau$, as suggested by the Onsager fluctuation–regression hypothesis, then since $\tau$ is usually $\sim 10^{-9}$ s when $\langle \hat{F} \rangle$ is a typical fast variable of extended thermodynamics [18, 19] the interval $0 \leqslant t < y_1^{-1}$ for which convergence of $a_0^*$ is proved in (21) will exceed the duration of most experiments.

### *3.1. Evaluation of the $b_p$ coefficients in the ansatz*

As observed above, we expand (22) in a Maclaurin series in powers of $t$ and determine the coefficients $\{b_p\}$ to make the coefficient of $t^{2n}$ in the expansion of (22) equal $c_n^*$. The $\{c_n^*\}$ used here are obtained from the truncation model which assumes $f_j = 0 = \Delta_j$ for $j \geqslant 5$, and thus $c_n^*$ for $n > 4$ is calculated from (17). Only $c_0^*, \ldots, c_4^*$ agree exactly with the $\{c_n\}$ in (5$c$). This is sufficient to make (22) agree with (5$a$) and (5$c$) to $\mathrm{O}(t^8)$ as $t \to 0$.

The condition that the coefficient of $t^{2n}$ in the Maclaurin expansion of (22) equals $c_n^*$ is

$$c_n^* = \sum_{m=1}^{n+1} b_n (my_1)^{2(n+1-m)} E_{2(n+1-m)} / \{2(n+1-m)\}!. \tag{24}$$

$\{E_k\}$ here are the Euler numbers [20, chapter 23] which appear in the $t$-expansion of the hyperbolic secants. In (24), we use [20, section 23.1.15]

$$(-)^n E_{2n} = (4^{n+1}/\pi^{2n+1})(2n)!\gamma_n \qquad (n = 0, 1, \ldots) \tag{25$a$}$$

$$1 > \gamma_n > [1 + 3^{-1-2n}]^{-1}. \tag{25$b$}$$

Defining

$$\bar{c}_n \equiv (-)^n c_n^* (\pi^2/4)^n y_1^{-2n} \tag{26$a$}$$

$$\bar{b}_n \equiv (-)^{n-1} b_n (ny_1)^{2(1-n)} 4\pi^{-1} (\pi^2/4)^{n-1} \tag{26$b$}$$

we find that (24), after substitution from (25$a$), reduces to

$$\bar{c}_n = \sum_{m=1}^{n+1} \bar{b}_m m^{2n} \gamma_{n+1-m}. \tag{27}$$

The $\{\gamma_j\}$ here can be calculated from (25*a*) using tabulated values of the $\{E_{2n}\}$ [20, table 23.2] for $j < 30$, and $\gamma_j \cong 1$ for large $j$.

As remarked above, the set $\{c_n^*\}$ are being calculated according to (17) from the truncation model. Therefore, $\{c_n^*\}$ satisfy (18). Accordingly, from (20),

$$|c_{j+1}^*| \leqslant y_1^2 |c_j^*| \qquad (j \geqslant \bar{j}). \tag{28}$$

Equation (28) implies

$$|c_j^*| \leqslant y_1^{2(j-\bar{j})} |c_{\bar{j}}^*| \qquad (j > \bar{j}). \tag{29}$$

Now if

$$\zeta \equiv \max_{j \leqslant \bar{j}} \left( |c_j^*| / y_1^{2j} \right) \tag{30}$$

we have

$$|c_j^*| \leqslant \zeta y_1^{2j} \qquad (j \geqslant 0). \tag{31}$$

Referring to definition (26*a*), we have

$$|\bar{c}_j| \leqslant y_1^{2j} (\pi^2/4)^j y_1^{-2j} \zeta = \zeta (\pi^2/4)^j \qquad (\text{all } j). \tag{32}$$

This is the form in which we cast (20) in order to prove convergence of (22).

Having shown that the set $\{\bar{b}_n\}$ should satisfy (27), we can now use (27) and (32) to establish upper limits on the coefficients $\{b_p\}$ in (22), and these limits may be invoked to prove convergence of (22). Upper limits on $\{|\bar{b}_n|\}$ are obtained by applying induction to (27). We show first that $|\bar{b}_1|$ and $|\bar{b}_2|$ are less than limiting expressions indexed by $k$ $(k = 1, 2)$, to be established, and then prove that if these limits apply to $|b_p|$ for $1 \leqslant p < n$, then they hold for $|b_n|$.

Taking successively $n = 0, 1$ in (27), we find

$$\bar{c}_0 = 1 = \bar{b}_1 \gamma_0 \tag{33a}$$

$$\bar{c}_1 = \bar{b}_1 \gamma_1 + 4\bar{b}_2 \gamma_0 \tag{33b}$$

$\gamma_0$ and $\gamma_1$ in (33*b*) can be evaluated from (25*a*) with tabulated values $E_0 = 1 = -E_2$ which gives

$$\gamma_0 = E_0(\pi/4) = \pi/4 \tag{34a}$$

$$\gamma_1 = -E_2(\pi^3/32) = \pi^3/32. \tag{34b}$$

On using (34*a*) and (34*b*) in (33*a*) and (33*b*), we obtain

$$\bar{b}_1 = 4/\pi \tag{35a}$$

$$\bar{b}_2 = (1/\pi)\{\bar{c}_1 - (\pi^2/8)\}. \tag{35b}$$

From (32) and (35*b*), if $\zeta < \pi/2$, $|\bar{b}_2| < \pi^2/8$. If $\zeta \geqslant \pi/2$, $|\bar{b}_2| < \zeta\pi/4$ if $\bar{b}_2 > 0$ and $|\bar{b}_2| < \pi^2/8$ if $\bar{b}_2 \leqslant 0$. In both the latter cases, $|\bar{b}_2| < \zeta\pi/4$. These conclusions are summarized by

$$|\bar{b}_p| \leqslant (4\bar{\zeta}/\pi)(\pi^2/16)^{p-1} < (4\bar{\zeta}/\pi)(\pi^2/4)^{p-1} \qquad (p = 1, 2) \tag{36a}$$

$$\bar{\zeta} = \zeta \quad \text{if } \zeta \geqslant \pi/2 \qquad \bar{\zeta} = \pi/2 \quad \text{if } \zeta < \pi/2. \tag{36b}$$

Having shown that (36*a*) holds for $p = 1, 2$, we make the inductive assumption that (36*a*) holds for all $p < n$. Taking $n \geqslant 3$, we find that (25*b*) and (27) imply

$$|\bar{b}_n| \leqslant n^{-2(n-1)}\left[|\bar{c}_{n-1}| + \sum_{m=1}^{n-1} m^{2(n-1)}|\bar{b}_m|\right]. \tag{37}$$

Here we have solved (27) for $|\bar{b}_n|$ and then set $\gamma_n \to 1$ (an upper limit) and have replaced all terms on the right by their absolute values to obtain an upper limit. Into (37) we introduce the inductive assumptions based on (32) and (35*a*):

$$|\bar{c}_j| \leqslant \bar{\zeta}(\pi^2/4)^j < \bar{\zeta}(4/\pi)(\pi^2/4)^j \qquad (1 \leqslant j \leqslant n-1) \tag{38a}$$

$$|\bar{b}_j| \leqslant (4\bar{\zeta}/\pi)(\pi^2/4)^{j-1} \qquad (1 \leqslant j \leqslant n-1). \tag{38b}$$

Introducing (38*a*) and (38*b*) into (37), we find

$$\begin{aligned}|\bar{b}_n| &\leqslant n^{-2(n-1)}\bar{\zeta}(4/\pi)\left[(\pi^2/4)^{n-1} + \sum_{m=1}^{n-1}(\pi^2/4)^{m-1}\right] \\ &= n^{-2(n-1)}(4\bar{\zeta}/\pi)(\pi^2/4)^{n-1}\{1-(4/\pi^2)^n\}/\{1-(4/\pi^2)\} \\ &< n^{-2(n-1)}(4\bar{\zeta}/\pi)\{1-(4/\pi^2)\}^{-1}(\pi^2/4)^{n-1}. \end{aligned} \tag{39}$$

If $n \geqslant 3$, equation (39) implies that

$$|\bar{b}_n| < n^{-2(n-1)}(\pi^2/4)^{n-1}\Omega \qquad (n \geqslant 3) \tag{40a}$$

$$\Omega \equiv \bar{\zeta}(2.140\,92\ldots). \tag{40b}$$

Equation (40*a*) shows that if (38*b*) holds for $1 \leqslant j \leqslant n-1$, then it holds for $j = n$ and therefore, by induction, for all integers $j \geqslant 0$.

Equations (40*a*) and (26*b*) yield a limit for $|b_n|$

$$|b_n| = |\bar{b}_n|(ny_1)^{2(n-1)}(\pi/4)(4/\pi^2)^{n-1} < y_1^{2(n-1)}(\pi/4)\Omega. \tag{41}$$

To prove convergence of (22) for $t > 0$, we use (41) and the inequality

$$\operatorname{sech}(py_1t) \leqslant 2\exp(-py_1t) \qquad (p \geqslant 0). \tag{42}$$

Equations (41) and (42) imply that

$$|b_p|\operatorname{sech}(py_1t) < y_1^{2(p-1)}(\pi/2)\Omega\exp(-py_1t). \tag{43}$$

Introducing (43) into the sum of absolute values of the terms in (22), we have

$$a_0^b(t) < \sum_{p=1}^{\infty}(y_1t)^{2(p-1)}\exp(-py_1t)(\pi/2)\Omega \tag{44}$$

where $a_0^b$ denotes the sum in (22). This sum converges, since if $y \equiv y_1t$, we have

$$y^{2p}\mathrm{e}^{-py} = \exp\{-p(y - 2\ln y)\} \equiv M_p.$$

The minimum of $y - 2\ln y$ occurs at $y = 2$ where $2 - \ln 4 = 0.6137\ldots$. The sum in (44) is less than a sum of powers of $\exp(-0.6137)$ which converges. Therefore, equation (22) will converge absolutely for all $t \geqslant 0$. The convergence is uniform by the Weierstrass $M$-test since $\sum_p M_p$ converges. Therefore, we can integrate (22) term by term as we do in the following section.

## 4. Time integral of the new model and determination of $y_1$

If $\nu C(t)$ from (22) is substituted into (3*b*) and the resulting expression after term-by-term integration converges, we can adjust $y_1$ to make the model agree with, for example, a molecular dynamics determination of $\tau$, the relaxation time for $\langle \hat{F} \rangle$ (cf equations (3*a*) and (3*b*)). If the exponential model of (4) produces a good representation of $\nu C(t)$ at long times, the infinite time integral of (22) should predict $\tau \sim y_1^{-1}$.

### *4.1. Integration of the ansatz for $C(t)$*

Referring to the term of order $p$ in (22) and defining $z \equiv p y_1 t$, we have

$$\begin{aligned}\int_0^\infty t^{2p-2}\,\mathrm{sech}(p y_1 t)\,\mathrm{d}t &= \{2/(p y_1)^{2p-1}\}\int_0^\infty z^{2p-2}\mathrm{e}^{-z}[1 - \mathrm{e}^{-2z} + \mathrm{e}^{-4z} - \cdots]\,\mathrm{d}z \\ &= \{2/(p y_1)^{2p-1}\}(2p-2)![1 - 3^{1-2p} + 5^{1-2p} - 7^{1-2p} + \cdots] \\ &= \{2/(p y_1)^{2p-1}\}(2p-2)!\beta(2p-1). \end{aligned} \tag{45}$$

The function $\beta(n)$ is defined and discussed by Abramowitz and Stegun [20, section 23.2.22] where it is related to the Euler numbers $\{E_{2n}\}$. We have from [20],

$$\beta(n) \equiv \sum_{k=0}^{\infty} (-)^k (2k+1)^{-n} \qquad (n = 1, 2, \ldots) \tag{46a}$$

$$\beta(2n+1) = \{(\pi/2)^{2n+1}/2(2n)!\}|E_{2n}| \qquad (n = 0, 1, \ldots). \tag{46b}$$

Substituting from (46*b*) into the result of integrating (22) term by term and using (45), we obtain

$$\tau = \sum_{p\geqslant 1} (\pi/2 p y_1)^{2p-1} |E_{2p-2}| b_p. \tag{47}$$

To demonstrate absolute convergence of the sum in (47), we replace $b_p \to |b_p|$ and use (41) to obtain an upper limit on $|b_p|$. To obtain an upper limit on $|E_{2p-2}|$, we use (25*a*) and replace $\gamma_n$ by unity. Applying these limits to the sum of the absolute values of the terms in (47), we have

$$\tau < (\pi/2y_1)\Omega \sum_{p\geqslant 1} (2p-2)!\, p^{2p-1}. \tag{48}$$

Applying Stirling's approximation,

$$(2p-2)! \sim 2^{2p-2} p^{2p-2} \exp(-2p+2)$$

to (48), we obtain

$$\tau \lesssim (\pi/2y_1)\Omega \sum_{p\geqslant 1} p^{-1} 4^{p-1} \exp\{-2(p-1)\} \tag{49}$$

where $\Omega$ is defined in (40*b*). The terms in the sum in (49) are less than the corresponding terms in a geometric series in powers of $4/\mathrm{e}^2$ which converges. Therefore, we conclude that (47) converges absolutely.

### 4.2. Evaluation of $\tau$

Since (47) converges, it should be possible to use this equation to determine $y_1$. This determination should be effected by adjusting $y_1$ so that (47) agrees with an independent determination of $\tau$ via molecular dynamic evaluation of the correlation in (3*b*) or from experiment. In an experimental measurement of steady-state transport, a thermodynamic force $X$ (e.g. a temperature or concentration gradient) is applied to the system, and then a driving term $-(\Upsilon/\tau)X$ is added to the right-hand member of (3*a*) [18, 19]. $\Upsilon$ is the measured steady-state transport coefficient, and $(\Upsilon, \tau)$ can be determined [18, 19, 21] in certain cases from molecular models with the help of an application of Onsager reciprocity. Reference [21] reviews a number of examples.

If $\{|E_{2p-2}|\}$ are taken from tabulated values [20, table 23.2], we can write the first few terms of (47) in the form

$$\tau = (\pi/2y_1)b_1 + (\pi/4y_1)^3 b_2 + (\pi/6y_1)^5 5b_3 + (\pi/8y_1)^7 61b_4 + \cdots. \tag{50}$$

The $\{b_j\}_{j\leqslant 4}$ can be determined by solving (24) in which we use (10*a*)–(10*d*) for $c_1, \ldots, c_4$. We find

$$b_1 = 1 \tag{51a}$$

$$b_2 = \tfrac{1}{2}(-\Delta_1 + y_1^2) \tag{51b}$$

$$b_3 = \tfrac{1}{24}\tilde{\Delta}\Delta_1 - \Delta_1 y_1^2 + \tfrac{19}{24}y_1^4 \tag{51c}$$

$$b_4 = -(1/6!)\Delta_1\{\tilde{\Delta}^2 + \Delta_2\Delta_3\} + \tfrac{1}{2}(3y_1^2)b_3 - \tfrac{5}{24}(2y_1)^4 b_2 + (61/6)y_1^6 \tag{51d}$$

$$\tilde{\Delta} \equiv \Delta_1 + \Delta_2. \tag{51e}$$

Equations (51*a*)–(51*e*) can be extended to $b_j$ for $j > 4$ after making a corresponding extension of (10*a*)–(10*d*).

In the absence of molecular dynamic or reliable experimental determinations of $\tau$, we can use (50) to investigate for what values of $\tau$ there is a $y_1$ (adjusted to fit $\tau$) compatible with $\tau \sim y_1^{-1}$. This is the result we should obtain by putting $\tau = y_1^{-1}$ in (4) and substituting the result into (3*b*). If from (50) we find that there is a $\tau$ such that (47) predicts that $\tau \sim y_1$ then for this value of $\tau$ the long-time behaviour of the ansatz (22) is consistent with the Onsager fluctuation–regression hypothesis discussed in connection with (4) and widely used in non-equilibrium thermodynamics [13]. However, this value of $\tau$ may not agree with a computer evaluation of the correlation in (3*b*).

If we define $\tilde{y}_1 \equiv y_1/\Delta_1^{1/2}$, we can cast (50) and (51*a*)–(51*e*) in the form

$$\begin{aligned}\tau = (\pi/2y_1)\big[&1 + (\pi^2/64)(1-\tilde{y}_1^{-2}) + \tfrac{5}{72}(\pi/6)^4\{(\tilde{\Delta}/\Delta_1)\tilde{y}_1^{-4} - 24\tilde{y}_1^{-2} + 19\} \\ &+(\pi/4)^6\tfrac{61}{256}\big\{-\tfrac{1}{720}(\tilde{\Delta}^2 + \Delta_2\Delta_3)/\Delta_1^2\tilde{y}_1^6 \\ &+\tfrac{9}{48}(\tilde{y}_1^{-4}\tilde{\Delta}/\Delta_1 - 24\tilde{y}_1^{-2} + 19) - \tfrac{5}{3}(1-\tilde{y}_1^{-2}) + \tfrac{61}{720}\big\} + \cdots\big].\end{aligned} \tag{52}$$

If $\tilde{y}_1 = 1$ and $(\tilde{\Delta}/\Delta_1) = 5$ and $\Delta_3 = 0$, this gives

$$\begin{aligned}\tau &= (\pi/2y_1)\big\{1 + (\pi/4)^6\big(\tfrac{61}{5120}\big) + \cdots\big\} \\ &= (\pi/2y_1)1.0028 \sim y_1^{-1}.\end{aligned} \tag{53}$$

If $\Delta_3 > 0$ and $\tilde{y}_1 > 1$, this estimate of $\tau$ will increase, but (53) will continue to hold as to order of magnitude. If $\tilde{y}_1 < 1$, convergence slows in (52), and this equation ceases to provide a useful estimate, at least to the order included in (52).

As we shall point out in the next section, $\{b_j\}_{j\geqslant 2}$ characterize $\nu C(t)$ in the transition region between very short- and long-time behaviour. The latter, in the simple fluids postulated here, is not directly observed because $\tau \sim 10^{-9}$ s or less. If memory of short-lived correlations which relax during this transition period is lost, then $\nu C(t)$ may be given accurately by $\exp(-y_1 t)$ as $t \to \infty$ even if $y_1$ differs from the value which causes (52) to fit the $\tau$ calculated from (4) by molecular dynamics. The latter calculation does not provide for intervention of external fields producing loss of memory.

## 5. Discussion

Although the exponential decay model (4) for $C(t)$ is in accord with the Onsager fluctuation–regression hypothesis for non-conserved variables, and the latter hypothesis has been very successful in classical non-equilibrium thermodynamics [13, 22], equation (4) clearly fails as $t \to 0$, as shown in (6). A model for $C(t)$ consistent with both the long-time phenomenology and the short-time expansion in powers of $t^2$ given in (5*a*) should exhibit a cross-over from the behaviour of (5*a*) to an exponential decay at $t \to \infty$.

The ansatz in (22) achieves this, since $\nu C(t) \to 1 + O(t^2)$ as $t \to 0$, and $\nu C(t) \to 2b_1 \exp(-y_1 t)$ as $t \to \infty$. The coefficients $\{b_p\}$ in (22) are adjusted to make (22) agree with (5*a*) to $O(t^{2n})$ for a given finite $n$. For illustrative purposes we have taken $n = 4$ in the present paper. $\{\tilde{c}_p\}$ in (5*a*) for $p > 4$ has been replaced by the coefficients $\{\tilde{c}_p^*\}$ of the truncated Lee model of section 2.4. The truncated model sets $f_p = 0 = \Delta_p$ for $p > 4$ with $\Delta_p$ $(p \leqslant 4)$ the exact values consistent with a computer determination of $c_j$ $(1 \leqslant j \leqslant 4)$ in (10*a*)–(10*d*) which is used to calculate the $\Delta$s from the $c$s. The truncated model leads to (20) which is invoked to prove the convergence of (22) and its time integral. This model could be modified to the case of truncation at some higher order $p > 5$. However, the behaviour of (22) as $t \to 0$ is determined by $b_1$ and $b_2$ and as $t \to \infty$ by $y_1$. All the terms in (22) save the first two describe the cross-over region which covers such a short period that we can gain information about it only via a computer simulation. If (15) does not have a solution consistent with the exact, computer-generated values of $\Delta_1, \ldots, \Delta_4$ as boundary conditions, we still have an *ad hoc* model which fits the short- and long-time behaviour of $C(t)$, but it no longer fits into the systematic Lee formalism.

Whether a simulation of $\nu C(t)$ in the cross-over region would agree with a measurement if we could make one is an open question. If $C(t)$, when $\hat{F}$ is non-conserved, is exactly exponential at long times, the arguments of Lee in section 2.1 show that external fields must intervene during the cross-over to modify the dynamics. If such intervention destroys memory of the shorter-lived correlations $(p > 1)$ in (22) during the cross-over in which they relax, then the exponential decay at long times may effectively be more exact than it appears to be in (22). Thus, as far as comparison with actual laboratory measurements is concerned, nothing is demonstrably gained by truncating at an order higher than $p = 5$ which has been chosen here for illustrative purposes.

Success in fitting the exponential decay model at long times to a computer determination of $\tau$ does not prove that $C(t)$ actually decays exponentially as $t \to \infty$. One simulation [7] appeared to show exponential decay of the velocity autocorrelation function which was later shown [18] to fall off as $t^{-d/2}$. Without more convincing evidence from simulations using non-conserved variables, equation (22) improves on (4) only by explaining how we can have $\dot{C}(t) \to 0$ as $t \to 0$. The shorter relaxation frequencies in (22) do not all have to be integral multiples of a single parameter $y_1$. Equation (22) can be generalized if evidence is adduced requiring this.

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