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Non-linear reciprocity in extended thermodynamics from the Robertson formalism

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Abstract. Robertson has found a projection operator which, applied to the Liouville equation, yields an exact equation for $\sigma(x,t)$, the information-theoretic phase-space distribution. If the Robertson equation is multiplied by a set $\{\hat{F}_i\}$ of functions representing physical fluxes, odd under momentum reversal and even under configuration inversion, a set of evolution equations is obtained for time-dependent ensemble averages $\eta_i = \langle \hat{F}_i \rangle$ which are variables of extended thermodynamics. In earlier work, a perturbation calculation was developed, assuming just one variable η, for an operator $\hat{T}$ occurring in the Robertson equation. This calculation is extended here to the case where there are $\nu > 1$ variables. The coefficients in the evolution equations depend on $\{\eta_j\}$ and explicitly on time t at short times. It is shown here that these coefficients exhibit Onsager symmetry at long times, after the transient explicit t-dependence has disappeared, to $O(\eta^3)$.

PACS. 05.70.Ln Nonequilibrium and irreversible thermodynamics – 05.20.Jj Statistical mechanics of classical fluids – 05.60.Cd Classical transport

1 Introduction

Robertson [1] has obtained an exact statistical derivation of non-equilibrium thermodynamics from the Liouville equation. If the latter is satisfied by the phase-space distribution $\rho(x,t)$, one can find an operator, $\hat{P}_{\rm R}$, such that $\hat{P}_{\rm R}\dot{\rho} = \dot{\sigma}$, where $\sigma(x,t)$ is the information-theoretic distribution [2].

$$\sigma(x,t) = Z^{-1} \exp\left[-\beta \hat{H} - \sum_{i=1}^{\nu} \lambda_i \hat{F}_i(x)\right] \qquad (1)$$

which maximizes the information-theoretic entropy subject to matching conditions for the set $\{\dot{\eta}_i\}$ of thermodynamic state variables:

$$\eta_i = \langle \hat{F}_i \rangle = \int \sigma(x,t) \hat{F}_i(x) \mathrm{d}x \qquad (1 \leqq i \leqq \nu) \qquad (2)$$

where we integrate over phase space. The set $\{\lambda_i\}$ are determined to satisfy (2) identically. $\beta = (kT)^{-1}$ characterizes a heat reservoir with which the system is in thermal equilibrium, although it will not be in internal equilibrium unless the $\{\lambda_i\}$ vanish. Z is a normalizing factor. By operating on the Liouville equation with $\hat{P}_{\rm R}$, one obtains an exact equation for $\partial\sigma/\partial t$, with σ given by (1). Multiplying this equation by the functions $\{\hat{F}_i(x)\}$ and integrating over phase space, one gets exact evolution equations for the set $\{\dot{\eta}_i\}$ in the form of a sum of powers of the $\{\lambda_i\}$. As we shall see, these evolution equations can be cast in the form

$$\dot{\eta}_i = \sum_{j=1}^{\nu} L_{ij}(\{\lambda_p\}, t)\lambda_j(t) \qquad (1 \leqq i \leqq \nu). \qquad (3)$$

In a non-uniform system, the kinetic equations such as (3) are taken together with the hydrodynamic equations of energy, mass and momentum conservation to constitute "generalized hydrodynamic equations". Here the system is uniform and the particle number fixed. To conclude that T is fixed, we invoke the conventional definition of "heat bath" which is a system large enough so that its temperature is constant which exerts vanishingly-small forces on the molecules of the system with which it interacts. These forces induce an exchange of energy and momentum between system and heat bath at an unobservably slow rate during relaxation of the variables $\{\eta_i\}$. The observed relaxation process therefore occurs with energy and centre-of-mass effectively fixed. The extremely weak interaction with the heat bath does not perturb the system dynamics, permitting us to use the Liouville equation which applies to a system of fixed size and neglects interactions with the surroundings. Accordingly, for a system interacting with such a bath, the hydrodynamic equations trivially equate to zero the rates-of-change of densities of conserved quantities momentum and energy. In thermodynamics, in both equilibrium and non-equilibrium, temperature is operationally defined [3,4] as the reading of a thermometer

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with which the system is observed to be in thermal equilibrium or, failing this, by some other empirical procedure. Here, the heat bath plays the role of a thermometer, and the temperature of the system is the constant temperature T of the bath. The probability that during a given observation of relaxation of the set $\{\eta_i\}$ the energy is E is then proportional to exp $(-\beta E)$ with $\beta = (kT)^{-1}$. In a situation where a system is not in thermal equilibrium with a thermometer, *e.g.* a sound wave where T varies sinusoidally, the time-dependence of T is still inferred experimentally by comparing with absorption and dispersion measurements the result of postulating a sinusoidal time-dependence of T. Since T is fixed and the conservation equations trivial, equations (3) suffice to describe the observed relaxation of the system.

Equations (3) are phenomenological equations of non-equilibrium thermodynamics, relating fluxes $\dot{\eta}_i$ to thermodynamics forces. One can see that the $\{\lambda_i\}$ are proportional to thermodynamic forces by inserting (1) into the information-theoretic entropy [2],

$$S = -k \int \sigma \ln \sigma \, \mathrm{d}x. \tag{4}$$

The result obeys a Gibbs equation,

$$T\mathrm{d}S = \mathrm{d}E + \sum_i \lambda_i \beta^{-1} \mathrm{d}\eta_i \tag{5}$$

so that $\lambda_j \beta^{-1}$ is the thermodynamic force associated with the flux $\dot{\eta}_i$. Work terms or a term proportional to the chemical potential are absent because the system boundaries are fixed as is particle number N. Driving terms, proportional *e.g.* to a macroscopic temperature gradient are absent in (3) because the system is uniform.

If a driving force such as $-L_q T^{-1} \nabla T$ is added to (3) when η_i is component of $\mathbf{Q}$ = heat flux, positive definiteness of the irreversible entropy production calculated from (5) requires that (2) be written

$$\mathbf{Q} = -V^{-1} L_q \beta^{-1} \lambda_q + \cdots \tag{6}$$

where the ellipsis refers to terms proportional to other forces. There is thus an anti-symmetric Onsager coupling between the driving forces and the rates $\{\dot{\eta}_i\}$. This assures that if only low-frequency disturbances are propagating, so that the $\{\dot{\eta}_i\}$ can be neglected, equations (3) reduce to the classical phenomenological equations for coupled fluxes of *e.g.* heat and diffusion [5]. If $L_{ij} = L_{ji}$ obtains in (3), reciprocity will still obtain in the classical limit when the $\{\dot{\eta}_i\}$ can be neglected. Reference [6] gives a history of applications of reciprocity in extended thermodynamics. (See pp. 225–233.) Extended thermodynamics, in which the dissipative fluxes of classical non-equilibrium thermodynamics appear as variables, reduces to the classical formalism in the low-frequency limit in such a way that Onsager symmetry is preserved, assuming the classical form [6,7] with a new set of coefficients L'_{ij}.

We shall suppose in what follows that the variables $\{\eta_i\}$ are indeed the dissipative fluxes of classical non-equilibrium thermodynamics [7], *e.g.* components of $\mathbf{Q}$ or of the diffusion flow, and, accordingly, that the $\{\hat{F}_i\}$ are odd under reversal of particle momenta. The original reason [6] for introducing these variables is that reciprocity relations among the $\{L_{ij}\}$ can relate quantities susceptible of calculation from molecular models to others less readily calculable from models. In a steady state induced by constant driving forces, if reciprocity can be used in calculating the λ-dependence of the $\{L_{ij}\}$, we can predict non-linear effects in transport when the rate equations are solved for the $\{\eta_i\}$ in terms of the driving forces. There are a number of recent examples [8–11] of the use of extended thermodynamics to estimate non-linear effects in transport and chemical reactions. The emphasis in these works on reciprocity and molecular models diverges from the main stream in this field [12] which has been concerned more with the derivation of wave equations whose parameters can be fitted to experiment.

Our aim in the present paper is to determine conditions under which $L_{ij} = L_{ji}$ in (3) when the λ-dependence of these coefficients is taken into account. For simplicity, all the $\{\eta_i\}$ are taken to be odd under time-reversal and the $\{\hat{F}_i\}$ odd under reversal of particle momenta. Robertson [1] was unable to prove reciprocity when the L_{ij} depend on the $\{\lambda_p\}$. A specialization of his work [13] to equations having a structure typical of extended thermodynamics [6,12] including variables both odd and even under time-reversal, showed that symmetric reciprocity holds in general only if we neglect $O(\lambda_p)$ in the L_{ij}-coefficients coupling forces of the same parity, whilst anti-reciprocity holds to all orders in coefficients coupling forces of opposite parity under time-reversal. We consider here the Robertson formalism for terms in rate equations such as (3) which exhibit symmetric reciprocity in linear approximation to see whether at later times reciprocity-violating contributions to the $\{L_{ij}\}$ do not disappear. Typically $\mathbf{Q}$ in a simple liquid will relax in less than a nanosecond over which we do not actually make observations, and so non-linear reciprocity will be seen to hold over time scales of actual measurements and in the steady-state limit.

Physical examples of operators $\{\hat{F}_i\}$ have been given previously for heat flux [14], diffusion [15], and inelastic strain-rate [9]. These are discussed in the references cited, showing how the rates-of-change of the variables may be cast in the form (3). In a non-uniform system, they are coupled to gradients in such a way that they reduce to *e.g.* Fourier's law in the classical limit. In all these examples, $\hat{F}_i$ is even under configuration inversion, and so all our $\{\hat{F}_i\}$ will have this property, as well as being odd under particle momentum reversal.

We proceed to summarize the derivation of (3). Defining [1] $\hat{P}_{\mathrm{R}}$ by

$$\hat{P}_{\mathrm{R}}\, \chi = \sum_{j=1}^{\nu} (\partial\sigma/\partial\eta_j) \int \hat{F}_j\, \chi \, \mathrm{d}x \tag{7}$$

for arbitrary $\chi(x)$, we find [13] that the equation for $\dot{\sigma}$ assumes the form:

$$\dot{\sigma}(t) = -\mathrm{i}\hat{P}_{\mathrm{R}}(t)L\sigma(t) + \int_0^t \mathrm{d}t'\hat{P}_{\mathrm{R}}(t')\,\mathrm{i}\hat{L}\hat{T}(t,t') \times [1-\hat{P}_{\mathrm{R}}(t')]\,\mathrm{i}\hat{L}\sigma(t') \tag{8}$$

where $\hat{L}$ is the Liouville operator. $\hat{T}(t,t')$ is defined [1] to be the solution of

$$\partial\hat{T}(t,t')/\partial t' = T(t,t')[1-\hat{P}_{\mathrm{R}}(t')]\,\mathrm{i}\hat{L} \tag{9}$$

with $T(t,t)=1$. Multiplying (8) by $\hat{F}_i(x)$ and integrating over phase-space, we obtain [13]:

$$\partial\eta_i/\partial t = -\int_0^t \mathrm{d}t' \int \mathrm{d}x\ \mathrm{i}\hat{L}\hat{F}_i\{\partial\hat{T}(t,t')/\partial t'\}\sigma(t') \qquad (1 \leqq i \leqq \nu). \tag{10}$$

The first term on the right in (8) gives zero because the $\{\hat{F}_i\}$ are even under configuration inversion, causing the integrand in (7), *viz.* $\hat{F}_j\,\mathrm{i}\hat{L}\sigma$, to be odd.

Equation (8) belongs to a family of exact equations derivable [16] by projection operators from the Liouville equation. The $\hat{P}_{\mathrm{R}}$ have been so defined that the information theoretic σ, provided the $\{\eta_i\}$ are solutions of (10), is an exact solution of (8). In addition, η_i satisfies the result of replacing $\sigma \to \rho$ in (2). We thus have an exact closed set of phenomenological equations. The variables T, η_i chosen for the set should include all those whose values can be extracted from data to be analysed [16]. Alternative approaches, *e.g.* the one based on Zwanzig-Grabert projection operators [17], yield an equation for a distribution which would give the same set of $\{\eta_i\}$ exactly if we could find an exact solution to the equation corresponding to (8), a solution dependent on the moments. In general, to use such an equation, one needs a closure approximation in the form of an ansatz which, in some cases [18] has been calculated from $\sigma(x,t)$ Since non-linear effects are small, one can then not be sure that any predictions are not artifacts of the closure approximation. Since $\sigma(x,t)$ solves exactly equation (8), its use in closure is not an approximation.

In order to investigate reciprocity, we seek to expand the right-hand member of (10) in powers of the $\{\lambda_i\}$ which correspond to thermodynamic forces [13]. If only linear terms are kept, previous work [1,13] has shown that we extract (3) with $L_{ij}=L_{ji}$. Apparently [13] the higher terms in the expansion cannot be regrouped to preserve reciprocity when L_{ij} is λ-dependent, but we want explicit expressions for these terms to see whether non-linear reciprocity does not hold approximately or become valid under suitable conditions, *e.g.* at long times.

The perturbation expansion of (10) in powers of the $\{\lambda_j\}$ is effected by expanding $\partial\hat{T}/\partial t'$ and σ with $\partial\hat{T}_n/\partial t'$, σ_n, and $\hat{P}_{\mathrm{R}}^{(n)}$ the respective contributions which are $O(\lambda^n)$. thus, from (6):

$$\partial\hat{T}_n(t,t')/\partial t' = \sum_{k=0}^{n} \hat{T}_{n-k}(t,t')\left[\delta_{k0} - \hat{P}_{\mathrm{R}}^{(k)}(t')\right]\mathrm{i}\hat{L}. \tag{11}$$

These equations can be solved successively [19], starting with

$$\hat{T}_0^{\pm}(t-t') = \exp\left[\mp\mathrm{i}(t-t')\{1-\hat{P}_{\mathrm{R}}^{(0)}\}\mathrm{i}\hat{L}\right] \tag{12}$$

as we show in the following section. The higher-order $\hat{P}_{\mathrm{R}}^{(k)}$ are found by substituting the λ-expansions of $\partial\lambda_k/\partial\eta_j$, and σ into (7). Once the λ-expansions of the operators have been obtained, we have:

$$\{\partial\eta_i/\partial t\}^{(k)} = -\int_0^t \mathrm{d}t' \int \mathrm{d}x\ \mathrm{i}\hat{L}\hat{F}_i \times \sum_{j=0}^{k-1}\{\partial\hat{T}(t,t')/\partial t'\}^{(j)}\sigma_{k-j}(t'). \tag{13}$$

By carrying out the procedures sketched above to evaluate (13) for $k=1,2,3$, we can consider whether the non-linear terms on the right can be regrouped to exhibit symmetric reciprocity, particularly in the long-time limit.

The perturbation solution of (11) has been developed in detail [19] for the case $\nu=1$ where there is just one variable. In the following section we shall summarize the extension to $\nu>1$ and give explicit expressions for $\partial\hat{T}_k/\partial t'$ for $1 \leqq k \leqq 3$. This permits investigation of the $O(\lambda^3)$ terms in (10) which are the lowest order non-linear contributions and the lowest order [13] in which we may find violations of reciprocity. In Section 3, we examine in detail the right-hand member of (13) for $k=1,2$, showing that it vanishes for $k=2$ and exhibits reciprocity for $k=1$. In Section 4, we examine several $O(\lambda^3)$ contributions to $\partial\eta_i/\partial t$. These involve integrals of time correlations of the $\{\hat{F}_i\}$ which have a transient explicit time-dependence, *i.e.* in addition to their dependence on $\lambda(t)$, at short times. At times exceeding the relaxation times of fast variables, and therefore on the time scale of actual measurements, the transient t-dependence will disappear, and reciprocity will apply. In Section 5, a summary and discussion will be given. A comparison is made there with earlier approximate calculations which use different projection operators.

2 Perturbation calculation of the operator $\hat{\mathbf{T}}(\mathbf{t},\mathbf{t}')$

The leading term in the λ-expansion of $\hat{T}$, as given by Robertson [1] is $\hat{T}_0^{+}(\bar{t})$ with $\bar{t} \equiv t-t'$, as given in (12). Evaluation of the integral obtained by substituting $\hat{T}_0$ into (10) has been given earlier [20]. To consider higher terms $\hat{T}_k$ in the λ-expansion of (9), we need σ_k and $\hat{P}_{\mathrm{R}}^{(k)}$. A straightforward expansion of (1) yields, with $\rho_{\mathrm{c}}(x)$ the equilibrium canonical distribution:

$$\sigma_0 = \rho_c \tag{14a}$$

$$\sigma_1 = -\rho_c \Lambda \tag{14b}$$

$$\sigma_2 = \frac{1}{2}\rho_c(\Lambda^2 - \langle \Lambda^2 \rangle_0) \tag{14c}$$

$$\sigma_3 = -(1/6)\rho_c \Lambda^3 + \frac{1}{2}\rho_c \langle \Lambda^2 \rangle_0 \Lambda \tag{14d}$$

$$\Lambda \equiv \sum_i \lambda_i \hat{F}_i. \tag{14e}$$

The subscript zero on an angular bracket denotes an equilibrium canonical average calculated using ρ_c, and σ_k is $O(\lambda^k)$.

Since the $\{\lambda_i\}$ depend on $\{\eta_j\}$, we can expand λ_i in powers of the η-variables and then invert to obtain $\eta_j^{(k)}$, the $O(\lambda^k)$ term in the inverted expansion. This can be used to obtain $\lambda_{kj}^{(p)}$, the $O(\lambda^p)$ term in the expansion of $\lambda_{kj} \equiv \partial\lambda_k/\partial\eta_j$. This is done for $p = 2$ in Section 4. With this notation, we obtain from (4), for arbitrary integrable phase function $\chi(x)$:

$$\hat{P}_{\mathrm{R}}^{(0)}\chi = -\rho_c \sum_{j=1}^{\nu}\sum_{k=1}^{\nu} \lambda_{kj}^{(0)} \hat{F}_k \int \hat{F}_j \chi \mathrm{d}x \tag{15a}$$

$$\hat{P}_{\mathrm{R}}^{(1)}\chi = \sum_{j,k}\{-\sigma_1 \lambda_{kj}^{(0)} \hat{F}_k + \rho_c \lambda_{kj}^{(0)} \eta_k^{(1)}\} \int \hat{F}_j \chi \mathrm{d}x \tag{15b}$$

$$\hat{P}_{\mathrm{R}}^{(2)}\chi = \sum_{j,k}\{-\sigma_2 \lambda_{kj}^{(0)} \hat{F}_k + \sigma_1 \lambda_{kj}^{(0)} \eta_k^{(1)} - \rho_c \lambda_{kj}^{(2)} \hat{F}_k\} \int \hat{F}_j \chi \mathrm{d}x. \tag{15c}$$

With these results, we can seek a solution of (11) in the form [19]:

$$\hat{T}_n(t,t') = \sum_{k=1}^{n} \hat{\theta}_k(t,t')\hat{T}_{n-k}(t,t') \qquad (n \geqq 1). \tag{16}$$

Substitution from (16) into (11) yields a family of equations which may be solved successively for $\hat{\theta}_1,\ \hat{\theta}_2, \ldots$ subject to $\hat{\theta}_0 = 1$ and $\hat{\theta}_j(t,t') = 0$ for $j > 0$. The solutions [19] take the form:

$$\hat{\theta}_1(t,t') = \int_{t'}^{t} \hat{T}_0(t,t')\hat{P}_{\mathrm{R}}^{(1)}(t_1)\mathrm{i}L\hat{T}_0^{-1}(t,t_1)\mathrm{d}t_1 \tag{17a}$$

$$\hat{\theta}_2(t,t') = \int_{t'}^{t} \mathrm{d}t_1\, \hat{T}_0(t,t_1)\left[P_{\mathrm{R}}^{(2)}(t_1)\mathrm{i}\hat{L}\hat{T}_0^{-1}(t,t_1) - \hat{P}_{\mathrm{R}}^{(1)}(t_1)\mathrm{i}\hat{L}\hat{T}_0^{-1}(t,t_1)\hat{\theta}_1(t,t_1)\right]. \tag{17b}$$

Substitution of (17a, b) into (16) yields $\hat{T}_1$ and $\hat{T}_2$. These, in conjunction with (10), give $\partial\hat{T}_1/\partial t'$ and $\partial\hat{T}_2/\partial t'$. We do not need $\partial\hat{T}_3/\partial t'$ which does not appear in (13) when $k = 3$. Its absence in (13) stems from the fact that $\mathrm{i}\hat{L}\sigma_0 = 0$. Therefore, we do not evaluate $\hat{\theta}_3$.

3 Linear and quadratic terms in the evolution equation

Equations (12, 16), and (17a, b) give us $\hat{T}_0,\ \hat{T}_1$, and $\hat{T}_2$ which, with (11), permit us to expand $\partial\eta_i/\partial t$ in (10) to $O(\lambda^3)$. The $O(\lambda)$ term in (10) is, from (13) with $k = 1$:

$$\{\partial\eta_i/\partial t\}^{(1)} = -\int_0^t \mathrm{d}t \int \mathrm{d}x\ \mathrm{i}\hat{L}\hat{F}_i\{\partial\hat{T}_0(t,t')/\partial t'\}\sigma_1(t') \equiv I_1. \tag{18}$$

There is no additional term involving $(\partial\hat{T}_1/\partial t')\sigma_0$, since this is proportional to $\mathrm{i}\hat{L}\sigma_0 = 0$. Introducing σ_1 from (14b) and Λ from (14c), we have:

$$I_1 = \int_0^t \mathrm{d}t' \int \mathrm{d}x\ \mathrm{i}\hat{L}\hat{F}_i\rho_c(\partial\hat{T}_0/\partial t')\sum_j \hat{F}_j\lambda_j(t'). \tag{19}$$

ρ_c commutes with $\hat{L}$ and with $\hat{P}_{\mathrm{R}}^{(0)}$, in the latter case because the average of $\hat{F}_j$ is zero in equilibrium.

The evaluation of I_1 in (19) has been discussed at length in earlier work [20] which we summarize here. The term involving $\hat{P}_{\mathrm{R}}^{(0)}$ in the square racket in (11) vanishes when we substitute from (11) into (19) because this term is proportional to integrals of the type $\int \hat{F}_i\,\mathrm{i}\hat{L}\hat{F}_j\ \mathrm{d}x$ whose integrands are odd under momentum reversal. We are left with:

$$I_1 = \int_0^t \mathrm{d}t' \int \mathrm{d}x\ \mathrm{i}\hat{L}\hat{F}_i\rho_c\hat{T}_0(t,t')\mathrm{i}\hat{L}\sum_j \hat{F}_j\lambda_j(t'). \tag{20}$$

To simplify the calculation without loss of generality, we shall choose the operators $\{\hat{F}_j\}$ to be the particular set $\{\tilde{F}_j(x)\}$ which diagonalize the $O(\lambda^2)$ terms in the λ-expansion of the Helmholtz free energy, Φ. When the $\{\tilde{F}_j\}$ are used, all related quantities will have a tilde. We have

$$\Phi = -(2\beta)^{-1}\sum_{i,j}\lambda_{i,j}^{(0)}\eta_i\eta_j \tag{21a}$$

$$-(\lambda^{(0)})_{ij}^{-1} = \langle \hat{F}_i\hat{F}_j\rangle_0 \tag{21b}$$

$$\tilde{F}_i \equiv \sum_{i,j}\Gamma_{ij}\hat{F}_j \tag{21c}$$

$$\tilde{\eta}_i = \sum_j \Gamma_{ij} j. \tag{21d}$$

The matrix Γ_{ij} diagonalizes $\lambda_{ij}^{(0)}$ so that, by (21b),

$$\tilde{\nu}_{ij} \equiv \langle \tilde{F}_i\tilde{F}_j\rangle_0 = 0 \quad (i \neq j) \tag{22a}$$

$$\langle \tilde{\Lambda}^2\rangle_0 = \sum_{i,j}\tilde{\nu}_{ij}\tilde{\lambda}_i\tilde{\lambda}_j. \tag{22b}$$

We shall use the model

$$\tilde{C}_{ij}(t) \equiv \langle \tilde{F}_i \exp(-\mathrm{i}\hat{L}t)\tilde{F}_j\rangle_0 = \tilde{\nu}_{ij}\exp(-\gamma_i t)\delta_{ij}. \tag{23}$$

The exponentially relaxing model for $\tilde{C}_{ij}(t)$ agrees [19] with the Onsager fluctuation-regression hypothesis. It does not give correctly $\lim_{t\to 0}\partial\tilde{C}_{ij}/\partial t$ in accord [19] with a widely perceived picture which requires a very short time before phenomenological irreversible thermodynamics can take over. In a dense fluid, $\tilde{C}_{ij}(t)$ can be evaluated *via* molecular dynamics. However, for analytical investigation of the t-dependence of I_1, we need [19] a model which is equivalent to specifying a mechanism for breaking the time-reversal symmetry. The diagonal character of (23) facilitates expression of the Fourier transform of (20) as a summable power series, as we shall demonstrate.

With the foregoing notation and the model (23), one can use an operator identity [20] to expand $\hat{T}_0(\bar{t})$ in the operators $\mathrm{i}P_{\mathrm{R}}^{(0)}\hat{L}$, so that we get

$$\begin{aligned}\hat{\zeta}(t) \equiv \langle \mathrm{i}\hat{L}\tilde{F}_i\hat{T}_0(\bar{t})i\tilde{F}_j\rangle_0 &= \langle \mathrm{i}\hat{L}\tilde{F}_i \exp(-\mathrm{i}\hat{L}t)\mathrm{i}\hat{L}\tilde{F}_j\rangle_0 \\ &+ \langle \mathrm{i}\hat{L}\tilde{F}_j \int_0^{\bar{t}} \mathrm{d}\xi \exp(-\mathrm{i}\hat{L}\xi)\mathrm{i}\hat{P}_{\mathrm{R}}^{(0)}\hat{L} \\ &\times \exp\{-\mathrm{i}\hat{L}(\bar{t}-\xi)\}\mathrm{i}\hat{L}\tilde{F}_j\rangle_0 + \ldots \end{aligned} \tag{24}$$

Each term in the right-hand member of (24) is a convoluted product of time integrations. This causes the Fourier transform of $\hat{\zeta}(t)$ to be proportional to a geometric series in powers of

$$\begin{aligned}\bar{\eta}_{ii} &\equiv (1/\tilde{\nu}_{ii}) \int_0^\infty \mathrm{e}^{\mathrm{i}\omega t}\{\partial\tilde{C}_{ii}(t)/\partial t\}\mathrm{d}t \\ &= -(1/\tilde{\nu}_{ii})\{\tilde{\nu}_{ii} + \mathrm{i}\omega\tilde{C}_{ii}(\omega)\}\end{aligned} \tag{25}$$

where we have used the model (23). The model gives us a sum of powers of $\bar{\eta}_{ii}$ rather than powers of a matrix. Summing the geometric series, we get for $\zeta(\omega)$, the Fourier transform of $\hat{\zeta}(t)$ [19,20]:

$$\zeta(\omega) = \mathrm{i}\omega\tilde{\nu}_{ii}\bar{\eta}_{ii}(\omega)/\{1+\bar{\eta}_{ii}(\omega)\}\delta_{ij} = \tilde{\nu}_{ii}\gamma_i\delta_{ij}. \tag{26}$$

On taking the inverse transform of $\zeta(\omega)$, we get:

$$(2\pi)^{-1}\int_{-\infty}^{\infty} \zeta(\omega)\mathrm{e}^{-\mathrm{i}\omega\bar{t}}\mathrm{d}\omega = \tilde{\nu}_{ii}\gamma_i\delta(\bar{t})\delta_{ij} \tag{27a}$$

$$\{\partial\eta_i/\partial t\}^{(1)} = I_1 = \int_0^{t+} \tilde{\nu}_{ii}\gamma_i\delta(t-t')\tilde{\lambda}_i(t')\mathrm{d}t' \tag{27b}$$

$$= \tilde{\nu}_{ii}\gamma_i\tilde{\lambda}_i(t). \tag{27c}$$

The upper integration limit in (27b) is chosen because it leads to the expected physical result that γ_i is the relaxation frequency of $\tilde{\eta}_i$, in accord with the Onsager fluctuation-regression hypothesis [20], as we proceed to show. A different choice of upper limit would produce an unphysical result.

From the matching condition (2), we have

$$\tilde{\lambda}_i = -(\tilde{\nu}_{ii})^{-1}\tilde{\eta}_i + O(\tilde{\eta}^3), \tag{28}$$

and so

$$\{\partial\tilde{\eta}_i/\partial t\}^{(1)} = I_1 = -\gamma_i\tilde{\eta}_i + O(\tilde{\eta}^3) \tag{29}$$

where $O(\tilde{\eta}^3)$ provides for the fact that a term linear in $\tilde{\lambda}$ can be non-linear in $\tilde{\eta}$. (29) shows that $\tilde{\eta}_i$ has the same relaxation time as $\tilde{C}_{ii}(t)$.

Since I_1 is diagonal, $\partial\tilde{\eta}_i/\partial t$ ($1 \leqq i \leqq \nu$) from (27) obviously exhibits Onsager reciprocity to terms linear in the $\{\tilde{\lambda}_i\}$. We have (*cf.* (21c):

$$\sum_i \tilde{\lambda}_i\tilde{F}_i = \sum_i \lambda_i\tilde{F}_i \tag{30a}$$

$$\tilde{\lambda}_i = \sum_i \Gamma_{ij}^{-1}\lambda_j \tag{30b}$$

where Γ_{ij} is symmetric because it diagonalizes the symmetric matrix $\lambda_{ij}^{(0)}$. To transform (27b) into the equation relating $\partial\eta_i/\partial t$ to the set $\{\lambda_i\}$, we multiply $-\gamma_i\delta_{ij}$ from the right and left by Γ^{-1}, obtaining a symmetric matrix of linear phenomenological coefficients. This conclusion agrees with earlier results [1,13] which found that the phenomenological equations for $\{\partial\eta_i/\partial t\}$ exhibit symmetric Onsager reciprocity to terms linear in the forces $\{\lambda_j\}$.

We have still to consider $\{\partial\eta_i/\partial t\}^{(2)}$ which, from (13) obeys:

$$\begin{aligned}\{\partial\eta_i/\partial t\}^{(2)} = -\int_0^t \mathrm{d}t' \int \mathrm{d}x\, \mathrm{i}\hat{L}\hat{F}_i\{(\partial\hat{T}_1/\partial t')\sigma_1(t') \\ + (\partial\hat{T}_0/\partial t')\sigma_2(t')\}\end{aligned} \tag{31}$$

where from (11):

$$\partial\hat{T}_1/\partial t' = \hat{T}_1(t,t')[1-\hat{P}_{\mathrm{R}}^{(0)}(t')]\mathrm{i}\hat{L} - \hat{T}_0(t,t')\hat{P}_{\mathrm{R}}^{(1)}\mathrm{i}\hat{L}. \tag{32}$$

Consider

$$\hat{P}_{\mathrm{R}}^{(1)}\mathrm{i}\hat{L}\sigma_1 = -\hat{P}_{\mathrm{R}}^{(1)}\mathrm{i}\hat{L}\left(\rho_{\mathrm{c}}\sum_k \lambda_k\hat{F}_k\right). \tag{33}$$

This is a sum of terms, each proportional to an integral of the type

$$\int \hat{F}_w\,\mathrm{i}\hat{L}(\rho_{\mathrm{c}}\hat{F}_k)\mathrm{d}x = 0 \tag{34}$$

which vanish because the integrand is odd under momentum reversal. The integral in the contribution to (31) which involves $\partial\hat{T}_1/\partial t'$ reduces to

$$\begin{aligned}\int \mathrm{d}x\, \mathrm{i}\hat{L}\hat{F}_i\hat{\theta}_1(t,t')\{\partial\hat{T}_0(t,t')/\partial t'\}\sigma_1(t') \\ = \int \mathrm{d}x\, \mathrm{i}\hat{L}\hat{F}_i \int_{t'}^t \hat{T}_0(t,t')\hat{P}_{\mathrm{R}}^{(1)}(t_1)\cdots\end{aligned} \tag{35}$$

From (14b), we see that the factors multiplying the integrals $\int \hat{F}_j\chi\,\mathrm{d}x$ in $\hat{P}_{\mathrm{R}}^{(1)}$ are even in the $\{\hat{F}_j\}$. As shown in (24), $\hat{T}_0$ can be expanded in the operators $\mathrm{i}\hat{P}_{\mathrm{R}}^{(0)}\hat{L}$. When this operates on $\hat{P}_{\mathrm{R}}^{(1)}\cdots$, we get integrals involving odd powers of the $\{\hat{F}_i\}$ which vanish unless there occur in the same integrals odd numbers of $\hat{L}$-operators. These are odd under configuration inversion, and so the integral in (35) is zero. We are left with

$$\{\partial\eta_i/\partial t\}^{(2)} = -\int_0^t \mathrm{d}t' \int \mathrm{d}x\ \mathrm{i}\hat{L}\hat{F}_i\{\partial\hat{T}_0/\partial t'\}\sigma_2(t'). \quad (36)$$

From (14c), σ_2 is even in the $\{\hat{F}_j\}$. Thus $\hat{P}_{\mathrm{R}}^{(0)}\mathrm{i}\hat{L}\sigma_2 = 0$ because it is proportional to integrals of the type $\int \hat{F}_i\,\mathrm{i}\hat{L}\sigma_2\mathrm{d}x = 0$. We are left in (36) with an integral having the same structure as the one discussed in (35) which vanishes for the same reason. Accordingly,

$$\{\partial\eta_i/\partial t\}^{(2)} = 0. \quad (37)$$

In deriving (37) we have shown that if L_{ik} in (3) is expanded in powers of the λ_j with $L_{ik}^{(p)}$ the $O(\lambda^p)$ term, then $L_{ik}^{(0)} = L_{ki}^{(0)} =$ const., whilst $L_{ik}^{(1)} = 0$. $L_{ik}^{(0)}$ exhibits no explicit dependence on t, and so $p = 2$ denotes the lowest order in which such a t-dependence will appear.

4 Cubic terms and explicit time-dependence

Having examined the $O(\lambda)$ terms in (10) and shown that $L_{ik}^{(0)} = L_{ki}^{(0)}$, we proceed to calculate $\{\partial\eta_i/\partial t\}^{(3)}$ from (13). We shall find, in agreement with [1] and [13], that $L_{ik}^{(2)} \neq L_{ki}^{(2)}$ at short times. However, the initial explicit time-dependence of $L_{ik}^{(2)}$ disappears at times greater than the relaxation times of fast variables. At $t\to\infty$, the terms in $\{\partial\eta_i/\partial t\}^{(3)}$ can be grouped in such a way that $L_{ik}^{(2)}$ exhibits symmetric reciprocity in this limit.

From (13), we have:

$$\{\partial\eta_i/\partial t\}^{(3)} = -\int_0^t \mathrm{d}t' \int \mathrm{d}x\ \mathrm{i}\hat{L}\hat{F}_i\{(\partial\hat{T}_0/\partial t')\}\sigma_3(t') + (\partial\hat{T}_1/\partial t')\sigma_2(t') + (\partial\hat{T}_2/\partial t')\sigma_1(t')\}\cdot \quad (38)$$

The curly bracket has no term proportional to $\sigma_0(t')$ because $\partial\hat{T}_k/\partial t = (\cdots)\mathrm{i}\hat{L}$ and $\mathrm{i}\hat{L}\sigma_0 = 0$. Designating by I_{3k} $(0 \leqq k \leqq 2)$ the integral in (38) involving $\partial\hat{T}_k/\partial t'$, we shall take up each of these three integrals in turn.

Substituting for σ_3 from (14d) into (38), we let I_{30p} be the term in I_{30} whose integrand is proportional to Λ^p, so that $I_{30} = I_{301} + I_{303}$. We see immediately that

$$I_{301} = -\frac{1}{2}\langle\Lambda^2\rangle_0\, I_1 \quad (39)$$

where I_1 has been evaluated in (29). We have seen that I_1 can be expressed to $O(\lambda)$ as a sum of terms whose coefficients exhibit symmetric reciprocity which continues to hold if we multiply I_1 by $\langle\Lambda^2\rangle_0$. The remaining term in I_{30} is:

$$\begin{aligned} I_{303} &= (1/6)\int_0^t \mathrm{d}t' \int \mathrm{d}x\ \mathrm{i}\hat{L}\hat{F}_i(\partial\hat{T}_0/\partial t')\Lambda^3\rho_{\mathrm{c}} \\ &= (1/6)\sum_{pjk}\int_0^t \mathrm{d}t' \int \mathrm{d}x\ \mathrm{i}\hat{L}\hat{F}_i\hat{T}_0\,\mathrm{i}\hat{L}\hat{F}_p\hat{F}_j\hat{F}_k \\ &\quad\times \rho_{\mathrm{c}}\lambda_p(t')\lambda_j(t')\lambda_k(t') \\ &= -(1/6)\sum_{pjk}\int_0^t \mathrm{d}t'(\partial^2/\partial\bar{t}^2)C_3^{ipjk}(\bar{t}) \\ &\quad\times \lambda_p(t')\lambda_j(t')\lambda_k(t') + \cdots \end{aligned} \quad (40a)$$

$$C_3^{ipjk}(t) \equiv \langle\hat{F}_i\exp(-\mathrm{i}\hat{L}t)\hat{F}_p\hat{F}_j\hat{F}_k\rangle_0. \quad (40b)$$

The ellipsis in (40a) represents higher terms in the expansion of $\hat{T}_0$ which has previously been used in (24). The contribution of these higher terms not given explicitly in (40a) can be evaluated by Fourier transformation in the manner illustrated in (24–26). Once again we can work in terms of the set $\{\tilde{F}_j\}$ and cast the Fourier transform of the integrand in (40a) in the form:

$$\begin{aligned} \bar{\zeta}(\omega) &\equiv -\int_0^\infty \mathrm{e}^{\mathrm{i}\omega t}(\partial^2/\partial\bar{t}^2)\tilde{C}_3^{ipjk}(\bar{t})\mathrm{d}\bar{t} \\ &\quad\times\left[1 - \bar{\eta}_{ii}(\omega) + \bar{\eta}^2 - \cdots\right] \\ &= -\int_0^\infty \mathrm{e}^{\mathrm{i}\omega t}(\partial/\partial\bar{t})\tilde{C}_3^{ipjk}(\gamma_i - \mathrm{i}\omega)\mathrm{d}\bar{t} \end{aligned} \quad (41)$$

where $\tilde{C}_3^{ipjk}$ is obtained by putting $\hat{F}_j \to \tilde{F}_j$ in (40b). On inverting the transform, we get:

$$(2\pi)^{-1}\int_{-\infty}^\infty \bar{\zeta}(\omega)\{\exp(-\mathrm{i}\omega\bar{t})\}\mathrm{d}\omega = -\gamma_i\partial\tilde{C}_3^{ipjk}(\bar{t})/\partial\bar{t} + \partial^2\tilde{C}_3^{ipjk}/\partial\bar{t}^2. \quad (42)$$

Using the result (42) for the integrand in (40a), we have:

$$I_{303} = (1/6)\sum_{pjk}\int_0^t \mathrm{d}t'\left[-\gamma_i\partial\tilde{C}_3^{ipjk}(\bar{t})/\partial\bar{t} + \partial^2\tilde{C}_3^{ipjk}/\partial\bar{t}^2\right]\tilde{\lambda}_p(t')\tilde{\lambda}_j(t')\tilde{\lambda}_k(t'). \quad (43)$$

$\tilde{C}_3^{ipjk}(\bar{t})$ is invariant under a change of sign of $\bar{t}$ because the odd powers of $\bar{t}$ involve odd powers of $\hat{L}$ so that the phase-space integration of these terms gives zero. Therefore, the first term in the square bracket changes sign under $\bar{t}\to-\bar{t}$, and so the coefficient relating $\dot{\eta}_i(t)$ to $\lambda_j(t')$ will not have Onsager symmetry as defined in previous work [1,13] and seen in the terms linear in the $\{\lambda_j\}$. If we let $t\to\infty$ and set $\tilde{\lambda}_p(t') = \tilde{\lambda}_p(t-\bar{t})$, we can replace $\tilde{\lambda}_p(t-\bar{t}) \to \tilde{\lambda}_p(t)$ on the assumption that $C_3(\bar{t})$ rapidly approaches zero as $\bar{t}$ increases. Large $\bar{t}$ makes a negligible contribution to the integral in (43). Then

$$I_{303} \xrightarrow[t\to\infty]{} (1/6)\gamma_i\sum_{pjk}\tilde{C}_3^{ipjk}(0)\tilde{\lambda}_p(t)\tilde{\lambda}_j(t)\tilde{\lambda}_k(t). \quad (44)$$

$\tilde{C}_3^{ipjk}(0) = \langle \tilde{F}_i \tilde{F}_p \tilde{F}_j \tilde{F}_k \rangle_0$ is symmetric under permutation of any pair of indices. If we regroup the terms in (44), we can set:

$$I_{303} = \sum_k \tilde{L}_{ik}^{(2,303)} \tilde{\lambda}_k \tag{45a}$$

$$\tilde{L}_{ik}^{(2,303)} = (1/6)(\gamma_i + \gamma_k) \sum_{p,j} \tilde{C}_3^{ipjk}(0) \tilde{\lambda}_p \tilde{\lambda}_j - (1/6) \sum_{p,j} \tilde{C}_3^{ipjk} \gamma_p \gamma_j. \tag{45b}$$

Then $\tilde{L}_{ik}^{(2,303)} = \tilde{L}_{ki}^{(2,303)}$. Using the transformation (21d) together with (30b), we continue to get Onsager symmetry in the I_{30} contribution to the matrix $L_{ik}^{(2)}$ relating $\dot{\eta}_i$ to the set $\{\lambda_j\}$ (with no tilde over the symbols).

Next we take up the contribution to $L_{ik}^{(2)}$ from the terms proportional to $\partial \hat{T}_1/\partial t'$ in the integrand of (38). Substituting from (14c), we put these contributions in the form:

$$I_{31} = -\frac{1}{2} \int_0^t \mathrm{d}t' \int \mathrm{d}x \; \mathrm{i}\hat{L}\hat{F}_i (\partial T_1/\partial \bar{t}')(\Lambda^2 - \langle \Lambda^2 \rangle_0)\rho_\mathrm{c} = I_{310} + I_{312}. \tag{46}$$

Again, the integrand in I_{31p} is proportional to Λ^p. From (11), $\partial \hat{T}_1/\partial t' = (\cdots)\mathrm{i}\hat{L}$ and $\mathrm{i}\hat{L}\rho_\mathrm{c} = 0$. Thus

$$I_{310} = 0. \tag{47}$$

In the calculation of I_{312}, it is seen that $\partial \hat{T}_1/\partial t'$ involves operators proportional to $P_\mathrm{R}^{(0)}\mathrm{i}\hat{L}$ and $P_\mathrm{R}^{(1)}\mathrm{i}\hat{L}$. Since these, in operating on $\Lambda^2\rho_\mathrm{c}$, yield factors of the type

$$\int \hat{F}_j \mathrm{i}\hat{L}\Lambda^2 \rho_\mathrm{c} \mathrm{d}x = 0, \tag{48}$$

which vanish because the integrand is odd under configuration-space inversion, we are left with:

$$I_{312} = -\frac{1}{2} \int_0^t \mathrm{d}t' \int \mathrm{d}x \; \mathrm{i}\hat{L}\hat{F}_i \hat{\theta}_1(t,t')\hat{T}_0(t,t')\{\Lambda(t')\}^2 \rho_\mathrm{c}. \tag{49}$$

Using (17a) for $\hat{\theta}_1$ and the expansion for $\hat{T}_0$ introduced in (24), we find that all the terms in (49) have factors whose integrands are odd in either configuration or momentum space. Therefore,

$$I_{312} = 0. \tag{50}$$

The third and final contribution in (38), when we substitute for σ_1 from (14b), takes the form:

$$I_{32} = \int_0^t \mathrm{d}t' \int \mathrm{d}x \; \mathrm{i}\hat{L}\hat{F}_i (\partial \hat{T}_2/\partial t')\Lambda\rho_\mathrm{c}. \tag{51}$$

Terms in $\partial \hat{T}_2/\partial t'$ proportional to $\hat{P}_\mathrm{R}^{(k)}\mathrm{i}\hat{L}$ yield integrals with one $\hat{L}$-operator which vanish for the same reason as does the integral in (48). Thus

$$I_{32} = \int_0^t \mathrm{d}t' \int \mathrm{d}x \; \mathrm{i}\hat{L}\hat{F}_i \hat{T}_2(t,t')\mathrm{i}\hat{L}\Lambda\rho_\mathrm{c} = \sum_j \int_0^t \mathrm{d}t' \lambda_j(t') \int \mathrm{d}x \; \mathrm{i}\hat{L}\hat{F}_i \theta_2(t,t')\hat{T}_0(t,t')\mathrm{i}\hat{L}\hat{F}_j \rho_\mathrm{c}. \tag{52}$$

The term $\hat{\theta}_1\hat{T}_1$ in $\hat{T}_2$ gives zero because it involves integrals of the type which cause the vanishing of I_{31}. Referring to (17b) for $\hat{\theta}_2$, we find that the term in $\hat{\theta}_2$ involving $\hat{\theta}_1$ vanishes for the same reason as the term $\hat{\theta}_1\hat{T}_1$ in $\hat{T}_2$, and so

$$I_{32} = \sum_j \int_0^t \mathrm{d}t' \lambda_j(t') \int \mathrm{d}x \; \mathrm{i}\hat{L}\hat{F}_i \int_{t'}^t \mathrm{d}t_1 \hat{T}_0(t,t_1) \times P_\mathrm{R}^{(2)}(t_1)\mathrm{i}\,\hat{L}\hat{T}_0(t_1,t')\,\mathrm{i}\hat{L}\hat{F}_j\rho_\mathrm{c}. \tag{53}$$

Into (53), we put $P_\mathrm{R}^{(2)}$ from (15c). This expression involves $\eta_k^{(1)}$ and $\lambda_{kj}^{(2)}$ which satisfy (*cf.* 14b, 22a and 28):

$$\sum_k \lambda_{kj}^{(0)} \eta_k^{(1)} = \lambda_j \tag{54a}$$

$$\lambda_{jk}^{(2)} = -\frac{1}{2}\lambda_{jk}^{(0)} \sum_{r,w} (\lambda_{rw}^{(0)})^{-1} \lambda_r \lambda_w - \lambda_j \lambda_k + \frac{1}{2} \sum_{mprw} \lambda_{jm}^{(0)} C_3^{mprw}(0) \lambda_r \lambda_p \lambda_{wk}^{(0)}. \tag{54b}$$

These equations will continue to hold if we add a tilde to each symbol.

We proceed to collect the various contributions to I_{32} stemming from terms in $P_\mathrm{R}^{(2)}$. Denoting by $I_{32(p)}$ a contribution from the term in σ_p in the curly bracket of (15c), we have, after introducing the set $\{\tilde{F}_j\}$ and using Fourier transformations as is done in (24–27b), four contributions to I_{32}:

$$I_{32(0)} = \sum_j \int_0^t \mathrm{d}\bar{t} \tilde{\lambda}_j(t-\bar{t}) \int \mathrm{d}x \; \mathrm{i}\hat{L}\hat{F}_i \hat{T}_0(\bar{t}) \times \sum_k \tilde{\lambda}_{kj}^{(2)}(t-\bar{t})\tilde{F}_k \tilde{\nu}_{jj}\gamma_j = -\sum_j \int_0^t \mathrm{d}\bar{t} \tilde{\lambda}_j(t-\bar{t}) \tilde{\nu}_{ii}\tilde{\nu}_{jj}\gamma_i\gamma_j \tilde{\lambda}_{ij}^{(2)}(t-\bar{t}) \tag{55a}$$

$$I_{32(1)} = \sum_j \int_0^t \mathrm{d}\bar{t} \tilde{\lambda}_j(t-\bar{t}) \int \mathrm{d}x \; \mathrm{i}\hat{L}\hat{F}_i \hat{T}_0(\bar{t}) \times \sum_p \tilde{F}_p \tilde{\lambda}_p \rho_\mathrm{c} \sum_r \tilde{\lambda}_{jr}^{(0)} \tilde{\nu}_{rr}\gamma_r \lambda_r \delta_{rj} = -\sum_j \int_0^t \mathrm{d}\bar{t} \tilde{\lambda}_j^{(2)}(t-\bar{t}) \tilde{\nu}_{ii}\tilde{\nu}_{jj}\gamma_i\gamma_j \tilde{\lambda}_i(t-\bar{t}) \tag{55b}$$

$$I^{(0)}_{32(2)} = \frac{1}{2}\sum_j \int_0^t \tilde{\lambda}_j(t-\bar{t})\mathrm{d}\bar{t}\int \mathrm{d}x\ \mathrm{i}\hat{L}\hat{F}_i\hat{T}_0(\bar{t})\langle \Lambda^2\rangle_{0,t-\bar{t}} \times \sum_{k,j}\tilde{\lambda}^{(0)}_{kj}\tilde{F}_k\tilde{\nu}_{jj}\gamma_j = -\frac{1}{2}\int_0^t \tilde{\lambda}_j(t-\bar{t})\mathrm{d}\bar{t}\sum_j \tilde{\nu}_{jj}\tilde{\lambda}^2_j(t-\bar{t})\tilde{\nu}_{ii}\gamma_i^2 \qquad (55c)$$

$$I^{(2)}_{32(2)} = \frac{1}{2}\sum_j \int_0^t \mathrm{d}\bar{t}\,\tilde{\lambda}_j(t-\bar{t})\int \mathrm{d}x\ \mathrm{i}\hat{L}\hat{F}_i\hat{T}_0(\bar{t})\sum_{k,r}\tilde{\lambda}_k(t-\bar{t}) \times \tilde{\lambda}_r(t-\bar{t})\tilde{F}_k\tilde{F}_r\rho_c\sum_w \tilde{F}_w\tilde{\lambda}^{(0)}_{wj}\tilde{\nu}_{jj}\tilde{\gamma}_j = -\frac{1}{2}\sum_j\int_0^t \mathrm{d}\bar{t}\tilde{\lambda}_j(t-\bar{t})\sum_{k,r}\tilde{\lambda}_k(t-\bar{t})\tilde{\lambda}_r(t-\bar{t})\tilde{\gamma}_j \times \left[(\partial/\partial\bar{t})\tilde{C}^{ikrj}_3(\bar{t}) - \gamma_i\tilde{C}^{ikrj}_3(0) + \gamma_i\tilde{C}^{ikrj}_3(\bar{t})\right]. \qquad (55d)$$

Here $I^{(k)}_{32(2)}$, with $i = 0, 2$, represent, respectively, contributions from the $0(\tilde{\Lambda}^k)$ terms in σ_2.

Inspection of (55b, c) shows that in a steady state where external forces not included in (8) and (10) cause the set $\{\tilde{\lambda}_j(t)\}$ to become constant as $t \to \infty$, the time integrals in (55b, c) will exhibit a secular divergence in this limit. However, if we substitute from (54b) for $\tilde{\lambda}^{(2)}_{ij}$ in (55a), the terms exhibiting secular divergences are found mutually to cancel on addition of (55a-d). After the addition, we are left with the result:

$$I_{32} = -\frac{1}{2}\sum_{jpr}\int_0^t \mathrm{d}\bar{t}\ \tilde{\lambda}_j(t-\bar{t})\tilde{\lambda}_r(t-\bar{t})\tilde{\lambda}_p(t-\bar{t})\gamma_j \times \{(\partial/\partial\bar{t})\tilde{C}^{ijpr}_3(\bar{t}) + \gamma_i\tilde{C}^{ijpr}_3(\bar{t})\}\cdot \qquad (56)$$

Remembering that $\bar{t} = t - t'$, we see, as in (43) that the derivative $(\partial/\partial\bar{t})\tilde{C}^{ijpr}_3(\bar{t})$, which changes sign under $\bar{t} \to -\bar{t}$, spoils the Onsager symmetry of the coefficient relating $\dot{\tilde{\eta}}_i(t)$ to $\tilde{\lambda}_r(t')$. As $t \to \infty$, since $\tilde{C}^{ijpr}_3(\bar{t})$ is assumed to decrease rapidly with increasing $\bar{t}$, we can replace $\tilde{\lambda}_j(t-\bar{t}) \to \tilde{\lambda}_j(t)$. Then

$$I_{32} \xrightarrow[t\to\infty]{} \sum_{jpr}\frac{1}{2}\gamma_j\left[\tilde{C}^{ijpr}_3(0) - \gamma_i\int_0^\infty \tilde{C}^{ijpr}_3(\bar{t})\mathrm{d}\bar{t}\right] \times \tilde{\lambda}_j(t)\tilde{\lambda}_p(t)\tilde{\lambda}_r(t). \qquad (57)$$

$\tilde{C}^{ijpr}_3(0)$ is symmetric with respect to permutation of any pair of indices. We can interchange $r \leftrightarrow j$, causing the contribution of this term to the coefficient multiplying γ_j on the right to have $i \leftrightarrow j$ symmetry. The remaining terms in (57) can be regrouped, giving:

$$I_{32} = -\frac{1}{2}\sum_{jpr}\left[\gamma_r\tilde{C}^{irpj}_3(0) - \gamma_r\int_0^\infty(\gamma_i\tilde{C}^{ijpr}_3(t) + \gamma_j\tilde{C}^{jipr}_3(t))\mathrm{d}t + \gamma_p\gamma_r\int_0^\infty \tilde{C}^{ripj}_3(t)\mathrm{d}t \times \tilde{\lambda}_j\tilde{\lambda}_p\tilde{\lambda}_r\right](t\to\infty) \qquad (58)$$

where the terms have been re-arranged in a manner resembling (45b), followed by the interchange $j \leftrightarrow r$ in the first integral on the right and $j \leftrightarrow p$ in the second integral.

If we pull out $\tilde{\lambda}_j$ in (58), the coefficient of this factor has $i \leftrightarrow j$ symmetry which is retained if we use (21c). Taking into account (39, 44, 47, 50) and (58), we get after adding all these contributions to I_3,

$$L^{(2)}_{ik} = L^{(2)}_{ki} \qquad (t\to\infty). \qquad (59)$$

Thus the non-linear Onsager symmetry, which is violated at short t in (56), holds at times greater than the time for $\tilde{C}^{ijpr}_3(t)$ to relax to zero, if the relaxation times for $\tilde{C}_{ij}(t)$ and $\tilde{C}^{ijpr}_3(t)$ are comparable, the time for establishment of Onsager symmetry is the relaxation time for fast variables. this is generally short compared with the time of actual measurements, and so non-linear reciprocity should apply to phenomenological descriptions of measurements.

5 Summary and discussion

The present work follows earlier papers [19,20] which develop (11) as a perturbation approach to the calculation of $\hat{T}(t,t')$. Robertson [1] gave only an expansion of $\hat{T}$ in powers of t which is not useful in the steady-state $t \to \infty$ limit which is often the goal of transport theory. In [20] there has been developed the linear $O(\lambda)$ approximation to (10). The expression for $\{\partial\eta_i/\partial t\}^{(1)}$ for the case where $\nu = 1$ and η is the only fast variable has an integral involving $\hat{T}_0$ defined in (12). This integral is evaluated in [20] *via* the operator expansion used in (24) plus Fourier transformation, as discussed in (25–27b). This calculation was extended [19] to include $n = 1, 2$ in (11), again assuming just one variable η. One could see that the explicit time-dependence of phenomenological coefficients disappears as $t \to \infty$. Thus the usual extended thermodynamic formulations [12] which depend on time only through their dependence on the relaxing variables, will hold at long times, at least when there is just one fast variable.

The present paper extends the previous one [19] by taking $\nu > 1$, making it possible to cast (10) in the form (3). The coefficients L_{ik} in (3) can be expanded in powers of the $\{\lambda_j\}$. In order to use here the methods of [20] to calculate $L^{(0)}_{ik}$, the lowest order in λ, we have utilized the variable transformation (21c) and the model (23) for the time-dependence of $\tilde{C}_{ij}$. This facilitates the calculation sketched in (25–27b). With this model, we find no explicit t-dependence in $L_{ik}^{(0)}$, whilst $L_{ik}^{(0)} = L_{ik}^{(0)}$ so that reciprocity holds.

Having shown that $L_{ik}^{(1)} = 0$, *i.e.* that the contribution to L_{ik} linear in λ vanishes, we go on to calculate $L_{ik}^{(2)}$, the $O(\lambda^2)$ term. The latter is expressible in terms of integrals over finite time of correlation functions $\tilde{C}_{ij}(t)$ and $\tilde{C}_3^{ijpr}(t)$. These integrals depend explicitly on t and violate reciprocity save in the $t \to \infty$ limit. In that limit, the terms can be regrouped to make $L_{ik}^{(2)} = L_{ki}^{(2)}$.

It is of interest to compare this result with an earlier use [18] of the information-theoretic $\sigma(x)$ (1) as an approximation for $\rho(t)$ in evolution equations for the $\{\dot{\eta}_i\}$ derived *via* Zwanzig Grabert projection operators [17] from the Liouville equation. The work of Grabert [17] modified the original formalism of Zwanzig [21], which assumed a microcanonically, distributed, isolated, closed system, so that the canonical distribution ρ_c could hold in equilibrium after the Grabert modification. *Via* projection operators, the Zwanzig-Grabert procedure derives from the Liouville equation a kinetic equation for a distribution giving correctly a limited number of moments, as does the Robertson σ which satisfies the matching conditions (2). The Zwanzig kinetic equation is exact. However, to obtain a closed set of equations such as (3) for a finite set of moments corresponding to $\{\hat{F}_i\}$ in the present paper, one must have an approximate solution (closure) of the kinetic equation which is a function of the moments of the finite set. Such a closure can be used to express higher moments in terms of moments belonging to the set. Without such a closure, one can obtain only a hierarchy of coupled equations for an infinite set of moments. Whilst Zwanzig with his projection operators may be said to have pointed the way, Robertson produced a kinetic equation for σ to which the information-theoretic distribution (1) and the associated moment equations constitute an exact solution, and so the moment equations for the variables $\{\eta_i\}$ may be characterized as exact. In the Zwanzig formalism, there is no exact closure which can be used to express higher moments in terms of lower ones, although the information-theoretic function (1) has been used [18] to effect an approximate closure. The problem is then that a prediction *via* such a procedure of non-linear reciprocity at longer times may be an artifact of the closure approximation used.

Although the information-theoretic distribution (1) is not a solution of the kinetic equation obtained [17] *via* Zwanzig-Grabert projection operators, it may still give a good representation of higher moments in terms of lower ones. In the work of Grad [22], an ansatz was substituted into moments equations obtained from the kinetic theory Boltzmann equation [23] to express third- or fifth-order tensors in terms of pressure and heat flux. The Grad ansatz may be regarded [24] as a linearization of the information-theoretic distribution (1). This kind of closure works well in linear kinetic theory. Its use [18] in the Zwanzig-Grabert formalism leads to a prediction of reciprocity which holds to all orders in λ provided t is long enough so that the $\{L_{ij}\}$ depend on the $\{\lambda_p\}$ but not explicitly on time. the result [18] agrees with the present paper to $O(\lambda^3)$ which is as far as we go here.

Since the Robertson evolution equations (8) are exact, one should be able to give an exact proof of the symmetry of the coefficients $\{L_{ik}\}$. It has been possible to show that the L_{ik} are given in terms of time-correlation functions which are calculable in principle in dense systems *via* molecular dynamics. In practice, for analytical results valid at short times, we need models like (23). Use of these is equivalent to specifying a model for breaking of time-reversal symmetry. If methods of Grad [22] or Chapman-Enskog [23] are used to evaluate the relaxation frequencies $\{\gamma_i\}$, the present approach provides an extension to non-linear transport in dilute gases without solving the non-linear Boltzmann equation.

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