Generalized Onsager symmetry

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Onsager's symmetry theorem for transport near equilibrium is extended in two directions. A corresponding symmetry is obtained for linear transport near nonequilibrium stationary states, and the class of transport laws is extended to include nonlocality in both space and time. The results are formally exact and independent of any specific model for the nonequilibrium state.

I. INTRODUCTION

The long-time dynamics of many systems close to equilibrium is well described by a closed set of linear hydrodynamic equations for the local conserved densities (e.g., mass, energy, and momentum). The dissipative properties of these equations are characterized by a matrix of transport coefficients in the linear relationship of fluxes to appropriate thermodynamic forces. On the assumption that the decay of fluctuations for a fluid at equilibrium is also governed by the same linear equations, Onsager was able to relate the transport coefficients to properties of equilibrium correlations functions. More specifically, the transformation of the correlation functions under time translation and time reversal imply a symmetry of the transport coefficients, known as Onsager reciprocal relations.[1] The usual Onsager reciprocal relations are actually limited to systems asymptotically close to equilibrium. For example, they apply at the level of the Navier-Stokes equations for a simple fluid, but fail for the higher-order corrections to these equations. The reason for this failure has been discussed by McLennan,[2] who also derived the appropriate generalization of the Onsager relations for higher-order hydrodynamics. The analysis of the following sections is a straightforward extension of McLennan's work to nonequilibrium stationary states. The results are formally exact and assume only the existence of such hydrodynamic equations. The form of the latter is left quite general to allow for possible nonlocal spatial and temporal effects.

Let $\{\psi(1;t)\}$ be a set of phase functions with average $\{\xi(1;t)\}$ in some nonequilibrium state at time t,

$$\xi(1;t)\equiv\langle\psi(1;t)\rangle . \tag{1}$$

The notation is an abbreviation for $\xi(1)=\xi_\alpha(\mathbf{r})$ where $\mathbf{r}$ is a space point and α labels the set of hydrodynamic variables. These variables are identified by the requirement that they obey a closed set of equations on a sufficiently long time scale. Typically they are the local conserved densities, whose relaxation times increase with the wavelength of the spatial nonuniformity. Consequently, there is a time scale on which they dominate all other variables

with finite relaxation times. For fluids with broken symmetries (e.g., liquid crystals) there can be other variables, the order parameters, whose relaxation times also increase with wavelength.[3] Generally, the hydrodynamic variables are understood to include these also when appropriate. The dynamics of $\xi(1;t)$ is expected to be quite complex but, by assumption, there is a simpler closed dynamics for sufficiently long times,

$$\frac{\partial}{\partial t}\xi(1;t)+N[\xi,1;t]=0, \quad t\gg t_m . \tag{2}$$

Here $N[\xi;1;t]$ is the nonlinear functional of ξ defining the dynamics, and t_m is a characteristic microscopic time scale after which Eq. (2) applies. These are the macroscopic hydrodynamic equations. A careful derivation of such equations would also provide appropriate boundary conditions as well as the form of $N[\xi;1;t]$, but it is not necessary here to consider this difficult problem. The macroscopic stationary states are specified by hydrodynamic variables $\xi^{(0)}(1)$, that are solutions to the equations

$$N[\xi^{(0)};1]=0 . \tag{3}$$

For nonequilibrium states near a stable stationary state, the deviations $\delta\xi(1;t)=\xi(1;t)-\xi^{(0)}(1)$ can be obtained from (2) by linearization around the stationary state

$$\frac{\partial}{\partial t}\delta\xi(1;t)+M[\delta\xi;1;t]=0, \quad t\gg t_m \tag{4}$$

where now $M[\delta\xi;1;t]$ is a linear functional obtained from $N[\xi;1;t]$ by functional differentiation. Its dependence on the stationary-state variables $\{\xi^{(0)}\}$ has not been made explicit.

The linear laws (4) apply only for $t\gg t_m$. In Sec. II an alternative *exact* expression for $\delta\xi(1;t)$ is obtained in terms of the stationary-state correlation functions. Comparison of (4) with this latter result for $t\gg t_m$ provides the analog of Onsager's assumption on the decay of fluctuations in equilibrium. The problem of "initial slip," identified by McLennan as the reason for the failure of the usual form of Onsager's symmetry relations outside the Navier-Stokes domain, is noted in the present context.

Next, the transformation properties of the correlation functions under time translation and time reversal are used to impose constraints on $M[\delta\xi;1;t]$; these constitute the generalized Onsager symmetry. In Sec. V the results are summarized and an example of their application is discussed.

For the special case of linearization around equilibrium, the linear functional $M[\delta\xi,1;t]$ can be represented as a spatial convolution

$$M[\delta\xi,1;t]\rightarrow\int d\mathbf{r}\, m_{\alpha\beta}(\mathbf{r}-\mathbf{r}')\delta\xi_\beta(\mathbf{r}',t) \tag{5}$$

as a consequence of translational invariance in the equilibrium state. A Fourier representation of (5) is then quite natural and the linear laws become a linear set of algebraic equations. In contrast, nonequilibrium stationary states generally do not have translational invariance, and the Fourier representation provides no special advantage. Consequently, the Onsager symmetry relations obtained below are expressed in coordinate representation. Finally, it is noted that the general form (4) does not assume a gradient expansion so that problems related to possible divergence of such expansions[4] do not restrict the results obtained here.

II. LINEAR DYNAMICS NEAR STATIONARY STATES

The average values of the hydrodynamic variables $\xi(1;t)$ are given by Eq. (1),

$$\xi(1;t)=\langle\psi(1;t)\rangle=\int d\Gamma\,\rho(\Gamma)\psi(1;t) , \tag{6}$$

where Γ denotes a point in phase space and $\rho(\Gamma)$ is the distribution function specifying a particular state of the system. In general it is understood that the system is open, i.e., interacting with its surroundings. For suitable boundary conditions it is assumed that there exists a class of stationary states generically denoted by $\rho_0(\Gamma)$. The hydrodynamic variables in such a state, $\xi^{(0)}(1)$, are time independent. Next, we consider a class of nonequilibrium states linearized around $\rho_0(\Gamma)$,

$$\rho(\Gamma)=\rho_0(\Gamma)[1+\delta y(1)\bar{\psi}(1)] , \tag{7}$$

where $\bar{\psi}(1)\equiv\psi(1)-\xi^{(0)}(1)$, and $\delta y_\alpha(\mathbf{r})$ are arbitrary functions characterizing the degree of deviation from the given steady ensemble. A summation convention, e.g.,

$$y(1)\bar{\psi}(1)=\sum_\alpha\int d\mathbf{r}\,y_\alpha(\mathbf{r})\bar{\psi}_\alpha(\mathbf{r}) , \tag{8}$$

is employed here and below. The value $\delta\xi(1;t)$ can be calculated directly from (6),

$$\delta\xi(1;t)=C(1,2;t)\delta y(2)=C(1,2;t)C^{-1}(2,3;0)\delta\xi(3;0) . \tag{9}$$

Here, $C(1,2;t)$ is the stationary-state correlation function

$$C(1,2;t)=\langle\psi(1;t)\bar{\psi}(2;0)\rangle_s \tag{10}$$

and the brackets $\langle\ \rangle_s$ denote an average over the stationary state $\rho_0(\Gamma)$. Equation (9) is the desired exact result for $\delta\xi(1;t)$.

The connection between linear hydrodynamics around

a stationary state and the correlation functions is obtained from comparison of (9) and (4) for $t\gg t_m$,

$$C(1,2;t)=T_t(1,2)\chi(1,2), \quad t\gg t_m \tag{11}$$

where T_t satisfies the linear hydrodynamic equations

$$\frac{\partial}{\partial t}T_t+M[T_t;t]=0 , \tag{12}$$

$$T_t(1,2)\,|_{t=0}=\delta(1-2) . \tag{13}$$

The quantity $\chi(1,2)$ cannot be identified with $C(1,2;0)$ since Eq. (11) holds only for $t\gg t_m$. Instead, it is defined by

$$\chi(1,2)=\lim_{t\to\infty}T_t^{-1}(1,2)C(1,2;t) . \tag{14}$$

Equation (11) extends Onsager's hypothesis on the decay of fluctuations[5] to nonequilibrium steady states: fluctuations in a stable stationary state decay for long times according to the linear hydrodynamic equations for nonequilibrium states near stationarity.[6]

The symmetry properties of $C(1,2;t)$ impose constraints on $T_t(1,2)$ and hence M through Eqs. (11) and (12). The latter are the desired Onsager symmetry relations. However, the quantity $\chi(1,2)$ is also involved in these constraints and it is useful to explore its interpretation. The quantities $\delta\xi(1;t)$ and $C(1,2;t)$ can be decomposed into their hydrodynamic and "microscopic" parts,

$$\delta\xi(1;t)=\delta\xi_H(1;t)+\delta\xi_m(1;t) ,$$
$$C(1,2;t)=C_H(1,2;t)+C_m(1,2;t) , \tag{15}$$

where by definition $\delta\xi_m$ and C_m vanish for $t\gg t_m$, and the hydrodynamic parts are given by

$$\delta\xi_H(1;t)\equiv T_t(1,2)\delta\xi_H(2;0) ,$$
$$C_H(1,2;t)\equiv T_t(1,2)\chi(1,2) . \tag{16}$$

Equations (15) and (16) are no longer restricted to $t\gg t_m$, so $\chi(1,2)$ is identified as the initial value for the hydrodynamic part of the correlation function. Then $\delta\xi_H(1;0)$ can be expressed in terms of $\delta\xi(1;0)$ using (9),

$$\delta\xi_H(1;0)=\delta\xi(1;0)$$
$$+[\chi(1,2)-C(1,2;0)]C^{-1}(2,3;0)\delta\xi(3;0) . \tag{17}$$

The first term on the right side is the true value of $\xi(1;0)-\xi^{(0)}(1)$ in the initial ensemble (7). The proper initial value for the linear hydrodynamic equations differs from this by an amount proportional to $\chi(1,2)-C(1,2;0)$. This difference is referred to as initial slip, and is required to correct for the initial "boundary layer," $0\leq t<t_m$, during which the hydrodynamic equations do not apply. An argument of McLennan can be extended to show that $\chi(1,2)\rightarrow C(1,2;0)$ up to second order in a gradient expansion. Initial slip is therefore important only for sufficiently large spatial variations from the stationary-state values of $\xi^{(0)}(1)$.

III. GENERALIZED ONSAGER SYMMETRY

The Onsager symmetry is a property of M that follows from the transformation of $C(1,2;t)$ under time translation and time reversal. Since the correlation functions are defined for the stationary state they are invariant under time translation. In particular,

$$C(1,2;t)=C(2,1;-t) . \tag{18}$$

Next, time reversal is defined microscopically by $t \rightarrow -t$ and a change in sign of all momenta. Without loss of generality, the hydrodynamic variables may be chosen to have a definite parity of ± 1 under time reversal. The time dependence of $\psi(t)$ is generated by Hamilton's equation which are form invariant under time reversal. However, boundary conditions are required to maintain the stationary state ρ_0. Under time reversal ρ_0 transforms to another stationary state $\bar{\rho}_0$ with corresponding boundary conditions. These two states and boundary conditions are simply related by the sign change of all momenta. Therefore, we need to consider a related correlation function,

$$\bar{C}(1,2;t)= \int d\Gamma \, \bar{\rho}_0 \psi(1;t)\bar{\psi}(2;0) . \tag{19}$$

It is now understood that $\psi(1;t)$ has the boundary conditions appropriate for $\bar{\rho}_0$. It follows that $C(1,2;t)$ and $\bar{C}(1,2;t)$ are related by

$$C(1,2;t)=\tau(1,3)\bar{C}(3,4;-t)\tau(4,2) , \tag{20}$$

where $\tau(1,2)=\tau(1)\delta(1-2)$ and $\tau(1)=\pm 1$ is the parity. Equations (18) and (20) can be combined to give

$$C(1,2;t)=\tau(1,3)\bar{C}(4;3;t)\tau(4,2) . \tag{21}$$

For $t \gg t_m$, C and $\bar{C}$ can be replaced by their hydrodynamic parts. Consequently, (21) implies as well

$$C_H(1,2;t)=\tau(1,3)\bar{C}_H(4,3;t)\tau(4,2) . \tag{22}$$

Then, with (16) and an obvious matrix notation (22) can be written

$$T_t\chi=\tau(\bar{T}_t\bar{\chi})^{\dagger}\tau . \tag{23}$$

The symbol $\dagger$ denotes the transpose, and a bar over a matrix indicates the corresponding quantity associated with the correlation function $\bar{C}$. To be more explicit, consider first the case of time-local hydrodynamic equations. The linear transport operator then has the form

$$M[\delta\xi;1;t]= \int d2 \, M(1,2)\delta\xi(2;t) , \tag{24}$$

and (23) becomes

$$e^{-Mt}\chi=\tau(e^{-\bar{M}t}\bar{\chi})^{\dagger}\tau . \tag{25}$$

Differentiation of this equation yields

$$M\chi=\chi\tau\bar{M}^{\dagger}\tau . \tag{26}$$

Next, writing (25) for $2t$ yields

$$e^{-Mt}(e^{-Mt}\chi)=\tau(e^{-\bar{M}t}\bar{\chi})^{\dagger}\tau\,\tau(e^{-\bar{M}t})^{\dagger}\tau ,$$

$$e^{-Mt}\tau(e^{-\bar{M}t}\bar{\chi})^{\dagger}\tau=e^{-Mt}\chi\tau(e^{-\bar{M}t})^{\dagger}\tau ,$$

and therefore,

$$\tau\bar{\chi}^{\dagger}\tau=\chi . \tag{27}$$

Use has been made of $\tau^2=1$. Combining (26) and (27) gives the desired result

$$M\chi=\tau(\bar{M}\bar{\chi})^{\dagger}\tau . \tag{28}$$

This can be put in a more familiar form

$$L(1,2)=\tau(1,3)\bar{L}^{\dagger}(3,4)\tau(4,2) , \tag{29}$$

where $L=M\chi$. For the equilibrium state $\bar{L}=L$ and the result of McLennan is regained. If further the hydrodynamics is restricted to the Navier-Stokes domain, then $\chi(1,2) \rightarrow C(1,2;0)$ and Onsager's original form follows. Equation (29) represents the extension of these results to nonequilibrium stationary states.

IV. MEMORY EFFECTS

The hydrodynamic variables describe the dominant long-time dynamics because their relaxation times can be made large for large wavelengths. However, in practice some systems can have nonhydrodynamic relaxation times that are comparable to those for the hydrodynamic variables under typical experimental conditions. Examples include many rheological materials and supercooled fluids.[7] Even in simple atomic fluids there are dynamical effects (mode coupling) that have very slow relaxation rates. It is still possible in these cases for the long-time dynamics to have a dominant hydrodynamic part in the sense of Eq. (11), but this dynamics may be nonlocal in time.[8] The form (24) is then replaced by

$$M[\delta\xi;1;t]= \int_0^t d\tau \int d2 \, M(1,2;t-\tau)\delta\xi(2;\tau) . \tag{30}$$

In this form the system is said to have memory effects. The solution to the hydrodynamic equations now is most easily expressed in terms of the Laplace transform

$$R(z)\equiv \int_0^{\infty} dt \, e^{-zt}T_t=[z+M(z)]^{-1} , \tag{31}$$

where $M(1,2;z)$ is the transform of $M(1,2;t)$. The transform of (23) leads to

$$R(z)\chi=\tau[\bar{R}(z)\bar{\chi}]^{\dagger}\tau , \tag{32}$$

or, with $R(z)=z^{-1}[1-R(z)M(z)]$,

$$\chi-\tau\bar{\chi}^{\dagger}\tau=R(z)M(z)\chi-\tau[\bar{R}(z)\bar{M}(z)\bar{\chi}]^{\dagger}\tau . \tag{33}$$

With the mild requirement that $M(z)/z$ vanish for large z, Eq. (27) is regained and (33) becomes

$$R(z)M(z)\chi=\tau[\bar{M}(z)\bar{R}(z)\bar{\chi}]^{\dagger}\tau$$
$$=\tau[\bar{R}(z)\bar{\chi}]^{\dagger}\tau\,\tau[\bar{M}(z)]^{\dagger}\tau$$
$$=R(z)\chi\tau[\bar{M}(z)]^{\dagger}\tau ,$$

or,

$$M(z)\chi=\chi\tau[\bar{M}(z)]^{\dagger}\tau . \tag{34}$$

Combining (34) and (27) gives the Onsager symmetry relation for systems with memory,

$$L(1,2;z)=\tau\bar{L}^{\dagger}(1,2;z)\tau , \tag{35}$$

where $L(z)\equiv M(z)\chi$ in analogy to (29).

V. DISCUSSION

The primary results here are Eqs. (29), or their extension for fluids with memory (35). They express a relationship of the generator for dynamics near a stationary state to the corresponding generator for the time-reversed stationary state. For the special case of equilibrium, these two stationary states are the same and a simple symmetry condition on the matrix L is obtained. For nonequilibrium states, the time-reversed state typically represents a physically different but related state. The utility of generalized Onsager symmetries therefore depends on an ability to characterize the time-reversal properties of a given stationary state. No attempt has been given here to address this difficult problem, although some explicit results can be obtained from semiphenomenological Fokker-Planck models.[9] Also, the transformation properties of stationary states generated by external conservative fields are easily identified: the fields transform with the same parity as the observables to which they couple. Stationary states with dissipative processes have been modeled by dynamics with nonconservative forces, suitable for computer simulation,[10] and again the transformation under time reversal is easily identified. More realistically, systems interacting with reservoirs at their boundaries are difficult to analyze except in certain limits (e.g., the boundary-value problem for the Boltzmann equation[11]). However, it might be expected that a wide class of stationary states could be characterized primarily by the hydrodynamic variables themselves, such that $\bar{\rho}_0(\xi) = \rho_0(\bar{\xi})$. Then, for example, Eq. (29) would simplify to

$$M(\xi)\mathcal{X}(\xi) = \tau[M(\bar{\xi})\mathcal{X}(\bar{\xi})]^\dagger \tau . \tag{36}$$

Although the Onsager symmetry applies to the exact asymptotic dynamics for the systems, it can be used also as an important constraint on approximate models for such dynamics. To illustrate such applications, consider the case of a fluid under uniform shear flow. This stationary state has been studied in detail by computer simulation, and is generated by periodic boundary conditions in the local Lagrangian frame of the fluid. In this frame the Liouville equation has an additional inertial force proportional to the shear rate a.[12] In addition, a nonconservative force is employed to maintain constant temperature,

also proportional to the shear rate. It is then easily verified that $\bar{\rho}_0(a) = \rho_0(-a)$. The hydrodynamics around this stationary state is quite complex since the state is inhomogeneous. Furthermore, comparison with the computer simulation requires consideration of very-short-wavelength phenomena outside the Navier-Stokes domain. A model for this dynamics has been proposed[13] using the exact short-time dynamics for a fluid of hard spheres. The justification is based on the fact that hard spheres have finite momentum transport even over infinitesimal times. To check the validity of the Onsager symmetry for this model, first note that there is no initial slip, so $\mathcal{X}(1,2) = C(1,2;0)$. The short-time dynamics is then easily shown to give

$$M(1,3)\mathcal{X}(3,2) = \langle [\mathcal{L}_+(a)\xi(1)]\bar{\xi}(2);a \rangle , \tag{37}$$

where $\mathcal{L}_+(a)$ is the Liouville operator (in the local rest frame) for a shear rate a, and $\langle \ ;a \rangle$ denotes an average over the corresponding stationary state. The adjoint of $\mathcal{L}_+(a)$ is $-\mathcal{L}_-(a)$ (where the subscripts $\pm$ refer to the singular hard-sphere interactions for positive and negative times, respectively).[14] Also, a change of integration variable, $p_\alpha \rightarrow -p_\alpha$, for all momenta gives $\mathcal{L}_+(a) = -\mathcal{L}_-(-a)$ and $\langle \ ;a \rangle \rightarrow \langle \ ;-a \rangle$. Consequently, (37) can be written

$$M(1,3)\mathcal{X}(3,2) = \tau(1,3)\langle \bar{\xi}(3)[\mathcal{L}_+(-a)\xi(4)]; -a \rangle \tau(4,2) . \tag{38}$$

The average on the right side of (38) can be recognized as the transposed short-time dynamics for the time-reversed state $\overline{(M\mathcal{X})}^\dagger$, and therefore the Onsager symmetry (29) holds for this model.

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