Statistical mechanical theory for steady state systems.

VII. Nonlinear theory

Phil Attard
School of Chemistry F11, University of Sydney, New South Wales 2006, Australia

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The second entropy theory for nonequilibrium thermodynamics is extended to the nonlinear regime and to systems of mixed parity (even and odd functions of molecular velocities). The steady state phase space probability density is given for systems of mixed parity. The nonlinear transport matrix is obtained and it is shown to yield the analog of the linear Onsager-Casimir reciprocal relations. Its asymmetric part contributes to the flux and to the production of second entropy. The nonlinear transport matrix is not simply expressible as a Green-Kubo fluctuation equilibrium time correlation function. However, here the first nonlinear correction to the transport coefficient is given explicitly as a type of the Green-Kubo equilibrium time correlation function. The theory is illustrated by application to chemical kinetics. © 2007 American Institute of Physics. [DOI: 10.1063/1.2745300]

I. INTRODUCTION

This is the seventh paper in a series on a theory for nonequilibrium thermodynamics and statistical mechanics.1–6 A self-contained review of the theory up to the fifth paper has been given.7 Briefly, the theory is based on the second entropy, which is the entropy associated with the transition between macrostates. The steady state emerges as the state that maximizes the second entropy, just as the equilibrium state maximizes the first entropy. Accordingly, the nonequilibrium theory is cast in a form deliberately analogous to the ordinary equilibrium theory.8 Notable points of the theory include the proof of the Onsager regression hypothesis and reciprocal relations by maximizing the asymptotic form for the constrained second entropy,9 the explicit formulation of the phase space probability function for the steady state, and the consequent development of a nonequilibrium Monte Carlo simulation algorithm.5 Throughout the flux is treated as a constrained variable whose steady state value maximizes the second entropy, and care is taken to distinguish general relations from relations that hold only in the steady state,6 which distinction is overlooked in most prior works.

The point of the present paper is fourfold: (1) to generalize the second entropy formulation to the nonlinear regime, (2) to generalize the theory to variables of mixed parity (i.e., to remove the previous restriction that macrostates must be derived from phase space functions that are even in the molecular velocities), (3) to give a nonlinear version of Onsager’s reciprocal relations, and (4) to give an expression for the phase space probability density for a steady state system with driving forces of mixed parity. In addition, the nonlinear theory is briefly illustrated by application to chemical kinetics.

A number of previous variational theories for nonequilibrium thermodynamics have been formulated, both linear9–11 and nonlinear.14–26 The simplest theories commonly deal with the velocity of a macrostate and are based on an expression for the rate of first entropy production.9,10,14,15,17,21,22 This class includes the dissipation function originally given by Onsager (“principle of least dissipation”).9 In contrast the present constrained second entropy approach deals with the transition between macrostates in a time interval (coarse velocity) and does not invoke the rate of first entropy production.2 The remaining theories give the probability of a trajectory between states and invoke the so-called thermodynamic Lagrangian whose action is minimized by the optimum path. (Higher order second entropies can be defined for a trajectory,2 and these at least conceptually are equivalent to such thermodynamic Lagrangians.) This class of theories finds application as the variational formulation of the stochastic differential equations such as the generalized Langevin equation and the generalized Fokker-Planck equation.27,28 Almost all these thermodynamic Lagrangians are based on the original functional for the rate of first entropy production given by Onsager and Machlup.11 The latter approaches generalize the original functional by including nonlinear effects and also the curvature of the generalization coordinate space.16–20

The Onsager-Machlup functional was quantitatively tested with computer simulations in the preceding paper in this series,6 and it was found to be deficient at finite times. Computer simulations of a particular time correlation function (or conductivity) did not show the exponential decay predicted by the Onsager-Machlup functional11 (and also by the Langevin equation) at least not over the time scales simulated.6 These results cast doubt on the validity of the Onsager-Machlup functional11 and obviously also on those based on it.16,18–20 The fundamental problems are as follows: (1) it is not valid to treat the finite time interval that necessarily appears in the stochastic approach as if it were an infinitesimal, (2) the expression for the rate of first entropy production used by Onsager and Machlup11 and others14,15,17,21,22 is only valid in the optimum state and is not valid in the general constrained state, and (3) there can be no theory for the nonequilibrium state based solely on the first entropy.
Another variational principle for nonequilibrium steady states is that proposed by Evans and Baranyai.\textsuperscript{29,30} This is said to be a nonlinear generalization of Prigogine’s principle of minimum entropy production in which the latter is equated to the rate of phase space compression. The present author has previously argued that the principle of minimum entropy production is erroneous.\textsuperscript{6} He has also argued that the compression of phase space that occurs in nonequilibrium molecular dynamics simulations is an artifact of the non-Hamiltonian equations of motion due to the artificial Evans-Hoover thermostat\textsuperscript{31,32} that is used.\textsuperscript{7} (Real systems obey Hamilton’s equations of motion, under which phase space is incompressible.) While this thermostat does little damage in the linear regime, the algorithm cannot be considered reliable in the nonlinear regime in which flux and structure become coupled.

Besides variational approaches and stochastic differential equations, other theories for nonequilibrium thermodynamics have been pursued, including phenomenological approaches.\textsuperscript{33–36} In general these theories postulate certain axioms or relationships, which the authors consider plausible by analogy with equilibrium thermodynamics, assume localized equilibrium thermodynamic relationships, and invoke the first entropy. The consequences of these postulates and assumptions await justification with convincing experimental or molecular-level computational evidence. Hatano and Sasa\textsuperscript{37} used Langevin dynamics to derive a type of second law for transitions between steady states postulated earlier by Oono and Paniconi.\textsuperscript{33} The steady state probability function [Eq. (4) of Ref. 37] is assumed independent of the past history of the work parameter, and the transition probability [Eq. (5) of Ref. 37] assumes constant work parameter. The results may possibly be valid for slowly varying work, in which regime experimental tests appear to have been performed,\textsuperscript{38} which is suggested by the fact that the analysis of the data used a probability distribution that also had no memory.\textsuperscript{39} (The general steady state probability was given in Paper V of this series, and transitions in the steady state were dealt with in Paper IV.\textsuperscript{4,5,7})

The nonequilibrium thermodynamic theory developed by the present author differs from these phenomenological approaches in that the second entropy that it is based on has a well-defined molecular basis [see Eq. (4) below], it has been shown to be consistent with known nonequilibrium theorems, and it has been tested with computer simulations.\textsuperscript{2,7}

Besides a nonequilibrium variational principle, this paper explores parity, nonlinearity, and phase space probability. The parity of a macrostate refers to whether or not its value changes sign when the molecular velocities are reversed, which is equivalent to reversing the direction of time. The previous second entropy analysis focused on variables all with even parity, whereas this paper generalizes the theory to the mixed parity case. Casimir\textsuperscript{40} first generalized Onsager’s reciprocal relation to the case of mixed parity in the linear case. Fox and Uhlenbeck\textsuperscript{41} treated the mixed parity case for stationary Gaussian-Markov stochastic processes. Grabert et al.\textsuperscript{42} analyzed the influence of fluctuations on nonlinear irreversible processes for systems of mixed parity, mainly in the context of the Fokker-Planck equation. In Ref. 43, computer simulations are used to explore the linear transport matrix for cases of mixed parity, with the emphasis on the relationship with time correlation functions, and on the influence of its asymmetric part.

This paper also analyzes the symmetry of the nonlinear transport matrix and derives a form of the Onsager reciprocal relation that agrees with that given by Grabert et al.\textsuperscript{42} There have been a number of other analyses and results presented for the nonlinear reciprocal relations.\textsuperscript{44–50} Incredibly, there have also been reports of experimental violations of the Onsager reciprocal relations in the nonlinear regime.\textsuperscript{51,52}

Finally, this paper gives the steady state phase space probability distribution for a subsystem that can exchange with reservoir variables of mixed parity. In Paper V of the series, the probability distribution was given for variables of even parity, and it was used to perform nonequilibrium Monte Carlo simulations for steady heat flow.\textsuperscript{7} Attard’s nonequilibrium phase space probability distribution differs from the Yamada-Kawasaki distribution,\textsuperscript{53,54} which (it was argued) does not correctly take into account exchange with the reservoirs.\textsuperscript{5} A modified thermostated form of the Yamada-Kawasaki distribution has been found to be computationally intractable.\textsuperscript{31,55,56}

### II. NONLINEAR SECOND ENTROPY

#### A. Isolated system

Denote the values of the collective quantities of interest (macrostates) at time \( t \) by a vector \( \mathbf{q}(t) \). The components could be, for example, the coordinates of a Brownian particle, the spatial distribution (moments) of conserved variables such as energy, number, or charge, the number of particular chemical species, a reaction coordinate, etc. Without loss of generality the zero of each component is chosen such that its average value vanishes, \( \langle \mathbf{q} \rangle = 0 \). The probability density of the macrostate is proportional to the exponential of the first entropy,\textsuperscript{8}

\[
\varphi(\mathbf{q}) \propto \exp \left( \mathcal{S}(\mathbf{q})/k_B \right),
\]

where \( k_B \) is Boltzmann’s constant. The thermodynamic force is defined as the entropy derivative,

\[
\mathbf{X}(\mathbf{q}) = \frac{\partial \mathcal{S}(\mathbf{q})}{\partial \mathbf{q}}.
\]

In the linear regime the first entropy is a quadratic form, \( \mathcal{S}(\mathbf{q}) = \text{const} + \mathbf{q} \cdot \mathbf{\epsilon} \cdot \mathbf{q} / 2 \), and hence the force is a linear function of the coordinates. The unconditional transition probability for \( \mathbf{q} \to \mathbf{q}' \) in time \( \tau \) is related to the second entropy by\textsuperscript{2,7}

\[
\varphi(\mathbf{q}',\mathbf{q}|\tau) \propto \exp \left( \mathcal{S}(\mathbf{q}')/\mathcal{S}(\mathbf{q}) \right)/k_B.
\]
\[ S^{(2)}(q', q|\tau) = k_B \ln \int d\Gamma_0 \delta(\hat{q}(\Gamma(\tau \Gamma_0)) - q') \times \delta(\hat{q}(\Gamma_0) - q), \]  
up to an arbitrary constant. The second entropy reduces to the first entropy upon integration

\[ S^{(1)}(q) = \text{const} + k_B \ln \int dq' \exp S^{(2)}(q', q|\tau)/k_B. \]  

The parity of a variable is defined in terms of its behavior under velocity reversal. If \( \mathbf{r} = (r^N, p^N) \) represents a point in phase space, then the conjugate point with all the velocities are reversed is \( \mathbf{r}' = (r^N, -p^N) \). If \( \hat{q}_i(\Gamma) = \hat{q}_i(\Gamma) \), then \( q_i \) has even parity and \( \epsilon_i = 1 \). Conversely, if \( \hat{q}_i(\Gamma) = -\hat{q}_i(\Gamma) \), then \( q_i \) has odd parity and \( \epsilon_i = -1 \). Loosely speaking, variables with even parity may be called position coordinates, and variables with odd parity may be called velocity coordinates. The parity matrix is diagonal with elements \( \{ \epsilon_q \} = \epsilon_q \delta_{ij} \). The parity matrix is its own inverse. \( \epsilon_q = 1 \). It commutes with the first entropy matrix \( \epsilon_q \delta_{ij} \), because there is no coupling between variables of opposite parity at equilibrium. \( q_i q_j \) = 0 if \( \epsilon_i \epsilon_j = -1 \). If variables of the same parity are grouped together, the first entropy matrix is block diagonal. The symmetry or asymmetry of the block matrices in the grouped representation is a convenient way of visualizing the parity results that follow.

The second entropy obeys the symmetry rules

\[ S^{(2)}(q', q|\tau) = S^{(2)}(q, q'|\tau) = S^{(2)}(q, q'|\tau). \]  

The first equality follows from time homogeneity: the probability that \( q' = q(\tau + t) \) and \( q = q(\tau) \) is the same as the probability that \( q = q(\tau - t) \) and \( q' = q(\tau) \). The second equality follows from microscopic reversibility: if the molecular velocities are reversed, the system retraces its trajectory in phase space.

Without assuming linearity, we may nevertheless take \( q' \) to be close to \( q \), which will be applicable for \( \tau \) not too large. Define

\[ E = E(q; \tau) = S^{(2)}(q, q'|\tau), \]
\[ F = F(q; \tau) = \frac{\partial S^{(2)}(q, q'|\tau)}{\partial q'} \bigg|_{q' = q}, \]

and

\[ \bar{G} = \bar{G}(q; \tau) = \frac{\partial S^{(2)}(q, q'|\tau)}{\partial q' \partial q} \bigg|_{q' = q}. \]

With these the second entropy may be expanded about \( q \), and to second order it is

\[ S^{(2)}(q', q|\tau) = E + (q' - q) \cdot \cdot F + \frac{1}{2} \bar{G} \cdot (q' - q)^2 \]
\[ = S^{(1)}(q) + \frac{1}{2} \bar{G}(q' - q + \mathcal{Q}^{-1}F)^2. \]  

Note that here and below, squared or juxtaposed vectors represent a dyad, and the centered dot and colon represent the scalar product. The final equality comes about because this is in the form of a completed square, and hence the reduction condition [Eq. (5)] immediately yields

\[ S^{(1)}(q) = E(q; \tau) - \frac{1}{2} \bar{G}(q; \tau)^{-1} : F(q; \tau)^2. \]  

The right-hand side must be independent of \( \tau \). The asymmetry introduced by the expansion of \( S^{(2)}(q', q|\tau) \) about \( q \) (it no longer obeys the symmetry rules [Eq. (6)]) affects the neglected higher order terms.

The second entropy is maximized by the most likely position, which from the completed square evidently is

\[ q(\tau) = q - \bar{G}(q; \tau)^{-1} F(q, \tau). \]  

The parity and time scaling of these coefficients will now be analyzed.

B. Parity

In addition to the coefficients for the nonlinear second entropy expansion defined above [Eqs. (7)–(9)], one can also define

\[ F^i(q; \tau) = \frac{\partial S^{(2)}(q_i, q_i'|\tau)}{\partial q'} \bigg|_{q' = q}, \]
\[ G^i_q(q; \tau) = \frac{\partial S^{(2)}(q, q_i'|\tau)}{\partial q_\tau \partial q} \bigg|_{q' = q}, \]

and

\[ G^i_i(q; \tau) = \frac{\partial S^{(2)}(q, q_i'|\tau)}{\partial q_\tau \partial q} \bigg|_{q' = q}. \]

Under the parity operator, these behave as

\[ E(q; \tau) = E(q; \tau), \]
\[ F(q; \tau) = \bar{G}^i(q; \tau), \]
\[ G^i_i(q; \tau) = \bar{G}(q; \tau), \]

and

\[ G^i_i(q; \tau) = \bar{G}^i_i(q; \tau) \tau = \bar{G}^i_i(q; \tau) \tau. \]

The matrices \( \bar{G}^i \) and \( \bar{G}^i_i \) are symmetric. If all the variables have the same parity, then \( \epsilon_q = \pm 1 \), which simplifies these rules considerably.

C. Time scaling

Consider the sequential transition \( q_1 \rightarrow q_2 \rightarrow q_3 \). One can assume Markovian behavior and add the second entropy separately for the two transitions. In view of the above results, in the nonlinear regime the second entropy for this may be written as

\[ S^{(2)}(q_1, q_2, q_3|\tau, \tau) \]
\[ = S^{(2)}(q_3, q_2, q_1|\tau, \tau) + S^{(2)}(q_2, q_1|\tau, \tau) - S^{(1)}(q_2) \]
\[ = \bar{G}^i_i(q_1; \tau, \tau) \tau [q_2 - q_1] + F^i(q_1; \tau, \tau) \cdot [q_2 - q_1] + E(q_1; \tau) \]
\[ + \frac{1}{2} \bar{G}^i_i(q_1; \tau, \tau) \tau [q_2 - q_1]^2 + F^i(q_1; \tau, \tau) \cdot [q_2 - q_1] + E(q_1; \tau) \]
\[ - S^{(1)}(q_1). \]  

The first three terms arise from the expansion of
$S^{(2)}(q_3, q_2 | \tau)$ about $q_3$, which accounts for the appearance of the daggers, and the second three terms arise from the expansion of $S^{(2)}(q_2, q_1 | \tau)$ about $q_1$. This ansatz is only expected to be valid for large enough $\tau$ such that the two intervals may be regarded as independent. This restricts the following results to the intermediate time regime.

The midpoint of the interval is $\hat{q}_2 = [q_3 + q_2] / 2$. The optimum point is that which maximizes the second entropy,

$$\frac{\partial S^{(2)}(q_3, q_2, q_1 | \tau, \tau)}{\partial q_2} \Bigg|_{q_2 = \hat{q}_2} = 0. \quad (21)$$

The difference between the optimum point and the midpoint is defined as

$$\lambda = \hat{q}_2 - q_2 = \lambda[q_3 - q_1]. \quad (22)$$

An explicit expression for $\lambda$ will be given below that shows that it is of order $\tau$. The second entropy for the transition $q_1 \rightarrow q_3$ is equal to the maximum value of that for the sequential transition,

$$S^{(2)}(q_3, q_2 | 2 \tau) = S^{(2)}(q_3, \hat{q}_2, q_1 | \tau, \tau). \quad (23)$$

This result holds insofar as fluctuations about the most probable trajectory are relatively negligible. Writing twice the left-hand side as the expansion about the first argument plus the expansion about the second argument, one has

$$2S^{(2)}(q_3, q_2 | 2 \tau) = \frac{1}{2} G(q_1, \tau; q_2) : [q_1 - q_3]^2 + F(q_1, \tau; \hat{q}_2) : [q_3 - q_1]^2 + \frac{1}{2} G(q_1, \tau; \hat{q}_2) : [q_3 - q_1]^2 + F(q_1, \tau; \hat{q}_2) : [q_3 - q_1] + E(q_1; \tau) \cdot q_2. \quad (24)$$

The right-hand side of Eq. (23) may be evaluated from Eq. (20), evaluated at the midpoint, $q_2 = \hat{q}_2$. This is equivalent to setting $\lambda = 0$, and so the results that immediately follow are valid to order $\lambda^0$. Accordingly, the sequential second entropy passing through the midpoint is

$$S^{(2)}(q_3, \hat{q}_2, q_1 | \tau, \tau) = \frac{1}{8} \left[ G(q_1; \tau) + G(q_3; \tau) : [q_3 - q_1]^2 + \frac{1}{2} F(q_1; \tau) + F(q_3; \tau) : \hat{q}_2 [q_3 - q_1] + E(q_1; \tau) + E(q_3; \tau) \right] + S^{(1)}(q_3) \right] + \frac{1}{16}[q_3 - q_1]^2 : \tilde{S}(q_1) + \tilde{S}(q_3). \quad (25)$$

Here the first entropy $S^{(1)}(\hat{q}_2)$ has been expanded symmetrically about the terminal points to quadratic order, with $\tilde{S}(q) = \partial^2 S^{(1)}(q) / \partial q^2 q$. Each term of this may be equated to half the corresponding one on the right-hand side of Eq. (24). From the quadratic term, one has

$$\frac{1}{8} \left[ G(q_1; \tau) + G(q_3; \tau) + \frac{1}{16} S(q_1) + S(q_3) \right] = \frac{1}{2} \left[ G(q_1; 2 \tau) + G(q_3; 2 \tau) \right]. \quad (26)$$

To satisfy this, $G$ must contain terms that scale inversely with the time interval and terms that are independent of the time interval. The expansion is nonanalytic. It follows that

$$G(q; \tau) = \frac{1}{\tau g_0(q)} + \frac{1}{\tau g_1(q)} + g_2(q) + \tilde{g}_3(q), \quad (27)$$

and that, in view of the parity rule [Eq. (18)],

$$g^{(1)}(q; \tau) = \frac{1}{\tau g_0(q)} - \frac{1}{\tau g_1(q)} + g_2(q) - \tilde{g}_3(q). \quad (28)$$

where $\tilde{g}_3(q) = 0$. It will be shown below that $g_1(q) = 0$. Note that neither $G(q; \tau)$ nor $G^{(1)}(q; \tau)$ can contain any terms in the intermediate regime other than those explicitly indicated, unless the first order contribution from $\lambda$ is included.

From the linear terms, one obtains for the second entropy forces

$$F(q_2; 2 \tau) = F(q; \tau) \quad \text{and} \quad F^\dagger(q_2; 2 \tau) = F^\dagger(q; \tau), \quad (30)$$

which imply that they are independent of the magnitude of the time interval. Hence

$$F(q; \tau) \sim f(q; \hat{\tau}), \quad f(q; \hat{\tau}) = f_0(q) + \hat{\tau} f_1(q) \quad (31)$$

and, from the parity rule [Eq. (17)],

$$F^\dagger(q; \tau) \sim f^\dagger(q; \hat{\tau}), \quad f^\dagger(q; \hat{\tau}) = f_0(q) - \hat{\tau} f_1(q). \quad (32)$$

For the case of a system where the variables only have even parity, this implies that $f_1(q) = 0$.

Finally,

$$\frac{1}{2} \left[ E(q_1; 2 \tau) + E(q_3; 2 \tau) \right] = \frac{1}{2} \left[ S^{(1)}(q_1) + S^{(1)}(q_3) \right]. \quad (33)$$

This equation implies that

$$E(q; \tau) \sim S^{(1)}(q), \quad (34)$$

to leading order.

These scaling relations indicate that in the intermediate regime, the second entropy [Eq. (10)] may be written as

$$S^{(2)}(q', q; \tau) = S^{(1)}(q) + \frac{1}{2} g_0(q) : [q' - q] + \frac{1}{\tau} g_1(q) \cdot f(q; \hat{\tau})^2. \quad (35)$$

(Here $g_1$ has been set to zero, as is justified below.) This shows that the fluctuations in the transition probability are determined by a symmetric matrix, $g_0$, in agreement with previous analyses.\(^{23,26,41}\)

The derivative of the left-hand side of the penultimate result is

$$\frac{\partial E(q; \tau)}{\partial q} = F(q; \tau) + F^\dagger(q; \tau) \sim 2 f_0(q). \quad (36)$$

Equating this to the derivative of the right-hand side shows that
\[ f_i(q) = \frac{1}{2} X(q). \]  

(37)

This relates the time-independent part of the natural nonlinear force to the thermodynamic force for a system of general parity in the intermediate time regime.

In view of the scaling of \( G^i(q; \tau) \), one is motivated to write

\[ G^i(q; \tau) \sim \frac{1}{|\tau|^2} g^0_i(q) + \frac{1}{|\tau|^2} g^1_i(q) + \frac{1}{|\tau|^2} g^2_i(q). \]  

(38)

In view of the parity rule [Eq. (19)], \( g^0_i \) and \( g^1_i \) are symmetric matrices and \( g^1_i \) and \( g^2_i \) are antisymmetric matrices.

The derivative of the second entropy force is

\[ \frac{\partial F(q; \tau)}{\partial q} = G^i(q; \tau) + g^2_i(q; \tau), \]  

(39)

which in the intermediate regime becomes

\[ \frac{\partial g_0^0(q)}{\partial q} + g^2_i(q; \tau) = \frac{1}{|\tau|^2} g^0_i(q) + \frac{1}{|\tau|^2} g^1_i(q) + \frac{1}{|\tau|^2} g^2_i(q) \]  

\[ + g^2_i(q) + g^1_i(q) + \frac{1}{|\tau|^2} g^0_i(q). \]  

(40)

Clearly then, the first two bracketed terms have to individually vanish. Since the first bracket contains two symmetric matrices, this implies that \( g^0_i(q) = -g^0_i(q) \), and since the second bracket contains a symmetric and an antisymmetric matrix, this also implies that \( g^1_i(q) = g^1_i(q) = 0 \). Further, since \( g^2_i(q) = S(q)/2 = \delta_i^0 g^0_i(q)/\partial q \), one can also conclude that \( g^2_i(q) = 0 \). Explicitly then, in the intermediate regime, one has

\[ G^i(q; \tau) = \frac{1}{|\tau|^2} g^0_i(q) + \frac{1}{2} S^i(q), \]  

(41)

\[ G^i(q; \tau) = \frac{1}{|\tau|^2} g^0_i(q) + \frac{1}{2} S^i(q), \]  

(42)

and

\[ G^i(q; \tau) = -\frac{1}{|\tau|^2} g^0_i(q) + \frac{1}{2} S^i(q), \]  

(43)

with

\[ g^1_i(q) = \delta_i^0 g^0_i(q), \]  

(44)

which will be used below.

In view of the reduction condition [Eq. (11)] and the above scaling of \( G \) and \( F \), one can, in fact, write to higher order

\[ E(q; \tau) \sim S^{(1)}(q) + \frac{1}{2} \tilde{g}^{(1)}_0(q) \cdot f(q; \tau)^2 + O(\tau^2). \]  

(45)

Since \( E(q; \tau) \) is an even function of \( \tau \), this shows that

\[ f_i(q) \cdot \tilde{g}^{(1)}_0(q) X(q) = 0. \]  

(46)

This says that \( f_i \) is orthogonal to the usual thermodynamic force \( X \) (using the inner product with metric \( \tilde{g}^0_0 \)).

It is always possible to write

\[ f_i(q) = g^{(0)}_0(q) \tilde{\Phi}(q) X(q). \]  

(47)

The matrix \( \tilde{\Phi} \) is underdetermined by this equation. If one takes the matrix to be antisymmetric,

\[ \tilde{\Phi}(q) = -\tilde{\Phi}(q)^T, \]  

(48)

then the quasizothgonality condition [Eq. (46)] is automatically satisfied. That same condition shows that

\[ \tilde{\Phi}(q) = g^{(0)}_0(q) \tilde{\Phi}(q) X(q), \]  

(49)

since \( f_i(q) = -g^{(0)}_0(q) X(q) \). Hence the most likely terminal position is

\[ \bar{q}(q, \tau) = q - \left| g^{(0)}_0(q) \right|^{-1} \left[ \frac{1}{2} X(q) + \tilde{\Phi}(q) \right] \]  

\[ = q - \frac{1}{2} g^{(0)}_0(q)^{-1} X(q) - \tau \tilde{\Phi}(q) X(q) \]  

\[ = q - 1 \bar{L}(q; \tau) X(q). \]  

(50)

The antisymmetric part of the nonlinear transport matrix is not uniquely defined (due to the nonuniqueness of \( \Phi \)). However, the most likely terminal position is given uniquely by any \( \bar{q} \) that satisfies Eq. (47).

The nonlinear transport matrix satisfies the reciprocal relation

\[ \bar{L}(q; \tau) = g^{(0)}_0(q) \tilde{\Phi}(q)^T X(q), \]  

(51)

These relations are the same as the parity rules obeyed by the second derivative of the second entropy [Eqs. (18) and (19)]. This effectively is the nonlinear version of Casimir’s generalization to the case of mixed parity of Onsager’s reciprocal relation for the linear transport coefficients \( \bar{g} \) [see also Eq. (63) below]. The nonlinear result was also given by Grabert et al. [Eq. (2.5) of Ref. 42], following the assertion of Onsager’s regression hypothesis with a state-dependent transport matrix.

One can define the symmetric and asymmetric most likely positions,

\[ q_\pm(q; \tau) = \frac{1}{2} \left[ q + \bar{q}(q; \tau) \pm \bar{q}(q; \tau) \right] \]  

\[ = \begin{cases} q - (|\tau|/2) g^{(0)}_0(q)^{-1} X(q) \\ -\tau g^{(0)}_0(q)^{-1} f_i(q). \end{cases} \]  

(52)

This shows that the even temporal development of the system is governed directly by the thermodynamic force, and that the odd temporal development is governed by \( f_i \).

In terms of the coarse velocity, \( \tilde{q}(q; \tau) = \left[ q - q \right]/\tau \), the most likely rate of production of the first entropy is

\[ \tilde{S}^{(1)}(q) = \bar{q}(q, \tau) \cdot X(q) \]  

\[ = -\frac{\tau}{2} \left[ X(q) + 2 \tilde{f}_i(q) \right] \cdot g^{(0)}_0(q)^{-1} X(q) \]  

\[ = -\frac{\tau}{2} X(q) \cdot g^{(0)}_0(q)^{-1} X(q). \]  

(53)

where the orthogonality condition [Eq. (46)] has been used. This shows that only the even part of the regression contributes to the most likely rate of first entropy production (as defined here), which is equivalent to retaining only the sym-
metric part of the transport matrix. This was also observed by Grabert et al. [Eq. (2.13) of Ref. 42].

It should be stressed that one cannot neglect the antisymmetric part of the transport matrix (equivalently \( f_1 \)) just because it does not contribute to the steady rate of first entropy production. Note that Casimir, on p. 348 of Ref. 40, argued that the antisymmetric component of the transport matrix had no observable physical consequence and could be set to zero. However, the present results show that the function makes an important and generally non-negligible contribution to the dynamics of the steady state (see Ref. 43 for further discussion of this point).

The value of the second entropy for an intermediate value of \( \tau \) is

\[
S^{(2)}(q', q | \tau) = S^{(1)}(q) + \frac{\tau}{2} g_0(q) : q^2 \\
+ \frac{\tau}{2} q \cdot [X(q) + 2 \mathcal{F}_1(q)].
\]  

One can identify the three terms on the right-hand side of the second equality. The first term, which is negative and independent of \( \tau \), represents the initial cost of erecting the static structure. The second term, which is negative and scales with \( \tau \), represents the ongoing cost of maintaining the dynamic order. The third term, which scales with \( \tau \) and in the most likely state is positive and larger in magnitude than the first, represents the ongoing first entropy produced by the flux.

The maximal value of the second entropy is

\[
\overline{S^{(2)}(q | \tau)} = S^{(2)}(\tilde{q}', q | \tau) \\
= S^{(1)}(q) + \frac{\tau}{8} g_0(q)^{-1} : [X(q) + 2 \mathcal{F}_1(q)]^2 \\
- \frac{\tau}{4} g_0(q)^{-1} : [X(q) + 2 \mathcal{F}_1(q)]^2 \\
= S^{(1)}(q) - \frac{\tau}{8} g_0(q)^{-1} : X(q)^2 - \frac{\tau}{2} g_0(q)^{-1} \mathcal{F}_1(q)^2.
\]  

In the final equality, one can see that due to the orthogonality condition, the even and odd parts of the regression contribute separately to the maximum value of the second entropy. Since the second entropy scales linearly with the time interval, one can say that in the steady state the rate of production of second entropy is positive, maximal, and constant. Note that in the constrained second entropy, a term involving \( x \) but not \( x' \) has been neglected throughout, when the symmetry was broken. The reduction condition is only satisfied to leading order, which is why this expression does not reduce exactly to the first entropy as it should. This does not affect the present physical interpretation of the various terms.

The optimum intermediate point of the sequential transition may be obtained by maximizing the corresponding second entropy. Using the expansion [Eq. (20)], the derivative is

\[
\frac{\partial S^{(2)}(q_1, q_2, q_3 | \tau, \tau)}{\partial \tilde{q}_2} \\
= \mathcal{F}(q_1; \tau) + \mathcal{G}(q_1; \tau)[q_2 - q_3] \\
+ \mathcal{F}(q_1; \tau) + \mathcal{G}(q_1; \tau)[q_2 - q_1] - X(q_2). 
\]  

Setting this to zero at the optimum point \( \tilde{q}_2 \) and writing it as the departure from the midpoint \( \tilde{q}_2 \), one has

\[
0 = \mathcal{F}(q_1; \tau) + \mathcal{F}(q_3; \tau) - X(q_3) - \overline{\delta(q_2)}[q_2 - q_3] \\
+ \frac{\tau}{2} \left[ \mathcal{G}(q_1; \tau) - \mathcal{G}(q_3; \tau) \right][q_2 - q_3] \\
+ \frac{\tau}{2} \left[ \mathcal{G}(q_1; \tau) - \mathcal{G}(q_3; \tau) \right][q_3 - q_1].
\]  

Hence to linear order in the differences in the intermediate regime, this is

\[
0 = \mathcal{F}(q_1; \tau) - \mathcal{F}(q_3; \tau) - \overline{\delta(q_2)}[q_2 - q_3] \\
+ \frac{2}{|\tau|} \overline{\delta(q_2)}[q_2 - \tilde{q}_2],
\]  

which has the solution

\[
\tilde{q}_2 - \tilde{q}_2 = \frac{\tau}{2} \left[ \mathcal{G}(q_1; \tau) - \mathcal{G}(q_3; \tau) \right][q_3 - q_1],
\]  

using Eq. (44). Hence one sees that the departure of the optimum point from the midpoint is of second order (linear in \( \tau \) and in \( q_3 - q_1 \)) and that \( \lambda \) is of linear order in \( \tau \). Neglecting it in the analysis above yields the leading contributions.

### D. Linear limit

In the linear regime, one has

\[
S^{(1)}(q) = \text{const} + \frac{1}{2} \overline{\delta q} : q^2.
\]  

Here for notational convenience \( \bar{q} = 0 \). From this the force is linear in the displacement, \( \mathcal{X}(q) = \overline{\delta q} q \).

There is no correlation between variables of opposite parity at a given instant at equilibrium; if \( \varepsilon_i \varepsilon_j = -1 \), then \( \langle q_i(t) q_j(t) \rangle_0 = 0 \). If one groups variables of the same parity, so that \( \varepsilon_i = 1, \quad i = 1, 2, \ldots, n_g \) and \( \varepsilon_i = -1, \quad l = n_g + 1, n_g + 2, \ldots, n_q + n_p \), then the first entropy matrix,

\[
\overline{\delta q} = \left. \frac{\partial S^{(1)}(q)}{\partial q} \right|_{q=0} = - \overline{\delta q} \overline{q}(t) \overline{q}(t) \overline{q}^{-1},
\]  

is block diagonal. One can readily see that all such block diagonal matrices commute with the parity matrix, \( \overline{\delta q} \overline{q} = \overline{q} \overline{\delta q} \). In fact, this result holds in any representation (irrespective of whether or not variables of the same parity are grouped together): any matrix that does not couple variables of opposite parity commutes with the parity matrix.

A related time correlation matrix may be defined

\[
\overline{Q}(\tau) = \kappa_T^{-1}(q(t + \tau) q(t))_0.
\]  

From the time reversible nature of the equations of motion, the matrix is “block asymmetric.”
\[ Q(\tau) = \varepsilon Q(\tau)^T \varepsilon = \varepsilon Q(-\tau) \varepsilon. \] (63)

This result will lead to a reciprocal relation for the linear transport matrix that is in essence equivalent to that given by Casimir.\(^4\)

The most general quadratic form for the second entropy is\(^2\)
\[ S^{(2)}(q^\prime, q|\tau) = \frac{1}{2} A(\tau):q^2 + q \cdot B(\tau)q^\prime + \frac{1}{2} A'(\tau):q^{'2}. \] (64)

(Since \(\langle q \rangle_0 = 0,\) linear terms must vanish.) In view of Eq. (6), the matrices must satisfy
\[ \varepsilon A(\tau) \varepsilon = A'(-\tau) = A(-\tau) \] (65)
and
\[ \varepsilon B(\tau) \varepsilon = B(-\tau)^T = B(-\tau). \] (66)

Also, as matrices of second derivatives with respect to the same variable, \(A(\tau)\) and \(A'(\tau)\) are symmetric.

Defining the symmetric matrix \(B(\tau) = B(\tau)\varepsilon \varepsilon B(\tau)^T\), the second entropy may be written as
\[ S^{(2)}(q^\prime, q|\tau) = \frac{1}{2} \varepsilon A(\tau) \varepsilon q^2 + q \cdot B(\tau)q^\prime + \frac{1}{2} A'(\tau):q^{'2} \]
\[ = \frac{1}{2} A(\tau):[\varepsilon q' + A(\tau)^{-1} B(\tau)q]^2 + \frac{1}{2} A'(\tau):q^{'2} \]
\[ - \frac{1}{2} q \cdot B(\tau) A(\tau)^{-1} B(\tau)q \]
\[ = \frac{1}{2} \varepsilon A(\tau) \varepsilon [q' + \varepsilon A(\tau)^{-1} B(\tau) \varepsilon q]^2 + S^{(1)}(q). \] (67)

The final equality results from the reduction condition. Using the quadratic form for the first entropy, this is
\[ S = A(\tau) - B(\tau) A(\tau)^{-1} B(\tau). \] (68)

The last two results are rather similar to the quadratic forms given by Fox and Uhlenbeck for the transition probability for a stationary Gaussian-Markov process [Eqs. (20) and (22)].\(^2\) Fox and Uhlenbeck\(^2\) did not identify the parity relationships of the matrices or obtain their time dependence explicitly, although the Langevin equation that emerges from their analysis and the Doob formula [their Eq. (25)] is essentially equivalent to the most likely terminal position in the intermediate regime obtained below.

The most likely position at the end of the interval is
\[ \tilde{q}(\tau) = -\varepsilon A(\tau)^{-1} B(\tau) \varepsilon q. \] (69)

Postmultiplying the most likely terminal position by \(k_0^{-1} q\) and taking the average yields
\[ Q(\tau) = \varepsilon A(\tau)^{-1} B(\tau) \varepsilon S^{-1}. \] (70)

This invokes the result, \(\langle \tilde{q}(q, \tau) \rangle_0 = \langle q(t+\tau) q(t) \rangle_0\), which is valid since the mode is equal to the mean for a Gaussian conditional probability [see also the discussion following Eq. (VI.24) of Ref. 6]. Using this the reduction condition may be written as
\[ A(\tau)^{-1}S = I - [A(\tau)^{-1}B(\tau)\varepsilon]^2 = I - [\varepsilon Q(\tau) S]^{-2}. \] (71)

In view of macroscopic reversibility, \(\varepsilon Q(\tau) = Q(\tau)^T \varepsilon\), this becomes
\[ A(\tau)^{-1}S = I - \frac{1}{2} q[A(\tau) + B(\tau) + \varepsilon A(\tau) + B(\tau)]\varepsilon q. \]
\[ = q - |q| X(q). \] (72)

This is symmetric, as it must be. One also has
\[ B(\tau) = [I - S Q(\tau) S Q(\tau)]^{-1} S Q(\tau) S^T, \] (73)
which has the correct asymmetry.

With these results, the second entropy becomes
\[ S^{(2)}(q^\prime, q|\tau) = \frac{1}{2} \varepsilon [q' + \varepsilon Q(\tau) S]^{2} + S^{(1)}(q). \] (74)

Hence it is evident that the most likely terminal position is
\[ \tilde{q}(q, \tau) = Q(\tau) S q, \] which of course could have been written down directly from the definition of the time correlation matrix. The matrix that controls the strength of the fluctuations is symmetric. That the symmetric part of the transport matrix controls the the fluctuations has been noted previously (see Sec. II F of Ref. 23).

Define
\[ Q^*(\tau) = \frac{1}{2} \varepsilon Q(\tau) + \varepsilon Q(\tau)^T = \pm Q^*(\tau). \] (75)

The matrix \(Q^*(\tau)\) is symmetric, and \(Q^*(\tau)\) is asymmetric. Since \(\varepsilon Q^*(\tau)\varepsilon = \varepsilon Q^*(\tau)\varepsilon\), then \(Q^*(\tau)\) must be block diagonal, and \(Q^*(\tau)\) must be block diagonal in the grouped representation. For small \(\tau\), one has
\[ Q^*(\tau) \sim -S^{-1} + |\tau| Q^* + \mathcal{O}\tau^2 \] (76)

and
\[ Q^*(\tau) \sim \tau Q^* + \mathcal{O}\tau^2. \] (77)

Hence one can show
\[ A(\tau) \sim \frac{1}{2|\tau|} Q^*(\tau)^{-1} + \mathcal{O}\tau^0 \] (78)

and
\[ A(\tau) + B(\tau) \sim \frac{1}{2}[S - \hat{N} S^* S + \mathcal{O}\tau]. \] (79)

In view of these results, the most likely terminal position is
\[ \tilde{q}(q, \tau) = -Q(\tau)S q - q \sim |q| [\hat{N} S^* S \tilde{X}(q) \]
\[ = q - |q| L_\tau \tilde{X}(q). \] (80)

Recall that in the grouped representation, \(Q^*\) contains nonzero blocks only on the diagonal and is symmetric, and that \(Q^*\) contains nonzero blocks only off the diagonal and is asymmetric. The transport matrix satisfies
\[ L_\tau \tilde{X}(q) = \varepsilon L_\tau (\tilde{x})^T \varepsilon \varepsilon = L_\tau (-\tilde{x})^T. \] (81)

These are called the Onsager-Casimir reciprocal relations (in the absence of external magnetic fields or Coriolis forces).\(^4\)

Direct evaluation of the general linear expression for the second entropy for a system of mixed parity [Eq. (64)] gives in the linear limit
\[ E(q; \tau) = \frac{1}{2} q[\hat{A}(\tau) + B(\tau) + \varepsilon (A(\tau) + B(\tau))]q, \] (82)
\[ F(q; \tau) = \varepsilon (A(\tau) + B(\tau))q. \] (83)
The left-hand side is the usual Green-Kubo formula for the
and
coefficients given above. Explicitly one has
These satisfy the appropriate parity rules.
One can verify explicitly from these, in the intermediate
regime and in the linear limit, the time scaling of the nonlinear
coefficients given above. Explicitly one has
and
are the
and

trace of the nonlinear coefficient matrix. Then solve for
the nonlinear transport matrix by successive substitution. Hence
these averages allow the evaluation of the first nonlinear cor-
rection to the transport matrix.
In the abstract it was pointed out that the nonlinear trans-
port matrix was not expressible as a simple Green-Kubo for-
ula. This assertion is confirmed by the explicit results ob-
tained here. Onsager originally used such a relation between
the linear transport matrix and the equilibrium time correla-
tion function to obtain the reciprocal relation. In the present
nonlinear case, the parity of the various matrices under time
and under velocity reversal was built in from the beginning
based on the formal requirements of the equilibrium trans-
formation. It was from these parity properties that the
reciprocal relation obeyed by the nonlinear transport matrix
was obtained.

E. Fluctuation formula for first nonlinear correction

In the linear regime, the transport matrix may be obtained
from an equilibrium time correlation function. This is
the Green-Kubo approach. Here a similar fluctuation formula
is given for the first nonlinear correction to the transport
matrix.
Denote the components of vectors, matrices, and tensors
by lowercase Greek letters and use the Einstein summation
convention over repeated indices. Defining
is straightforward to show that
It is assumed that

Now expand the nonlinear transport matrix to first order,

One can show that

The left-hand side is the usual Green-Kubo formula for the
linear transport coefficient. Hence to leading order this gives
the expected result.
To obtain the first order correction, one evaluates

It is straightforward to solve this set of equations for
For fixed
write everything as a matrix, multiply both sides by
the inverse of the pair correlation matrix, and evaluate the
trace of the equations to obtain an explicit expression for the

F. Reservoir

Now add an external reservoir that applies a thermody-
namic force
. If
is the state of the subsystem
under the internal change (i.e., as if it were isolated), then one
can let
be the state after the externally induced changes. By conservation the change in the reservoir is
and the change in the reservoir first entropy is
Even when the subsystem force is nonlinear, the reservoir force remains independent of
The second entropy then is a function of three con-
strained variables,
. The internal part, which accounts for the resistance to the flux, is as given
above; it characterizes the transition
. The external
part is entirely influenced by the reservoir, and it consists of
two parts: the equilibration with the reservoir for the initial
state
and the transition
. The singlet probability, representing the equilibration
with the reservoir, is

with the most likely state evidently satisfying
. [The subsystem thermodynamic force is
for the isolated system treated above it was denoted as
.] The exponent is the total first entropy and replaces the isolated system first entropy that appears in the
expression for the second entropy of the isolated system [Eq.
(10)].
The transition
is determined by one-half of the
external change in the total first entropy. The factor of 1/2
occurs for the conditional transition probability with no spe-
cific correlation between the terminal states, as this preserves
the singlet probability during the reservoir induced
transition. The implicit assumption underlying this is
that the conductivity of the reservoirs is much greater than
that of the subsystem.
The external change in the total first entropy is to qua-
dratic order,

It is straightforward to solve this set of equations for

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where a Taylor expansion about \( q \) has been invoked, and \( S_\omega(q) = d^2 S^{(1)}(q)/dq^2 \). Adding half of this to the conditional second entropy, the conditional total second entropy for the transition \( q \rightarrow q' \) in time \( \tau \) is

\[
S^{(2)}(\Delta' q, \Delta^0 q | q, \tau, X_r) = \frac{1}{2} G(q, \tau) [\Delta^0 q + G(q, \tau)^{-1} F(q, \tau)]^2 + \frac{1}{2} |X_r(q) - X_r| \cdot \Delta' q + \frac{1}{2} \Delta' q \cdot S_\omega(q) \Delta^0 q + \frac{1}{2} \Delta' q \cdot S_\omega(q) \Delta' q.
\]

(98)

Now find the most likely transition. The derivatives of the conditional total second entropy are

\[
\frac{\partial S^{(2)}(\Delta' q, \Delta^0 q | q, \tau, X_r)}{\partial \Delta' q} = G(q, \tau) [\Delta^0 q + G(q, \tau)^{-1} F(q, \tau)] + \frac{1}{2} S_\omega(q) \Delta^0 q
\]

and

\[
\frac{\partial S^{(2)}(\Delta' q, \Delta^0 q | q, \tau, X_r)}{\partial \Delta^0 q} = \frac{1}{2} [X_r(q) - X_r] + \frac{1}{2} S_\omega(q) \Delta^0 q + \frac{1}{2} S_\omega(q) \Delta^0 q.
\]

(100)

The vanishing of these give the most likely changes as

\[
\Delta^0 q = -2 G(q, \tau)^{-1} F(q, \tau) + X_r - X_r(q)
\]

(101)

and

\[
\Delta' q = S_\omega(q)^{-1} [X_r - X_r(q)] - \Delta^0 q.
\]

(102)

This last result ensures that \( X_r(q) = X_r \), which is as anticipated. Since \( X_r(q) = X_r \), this also implies \( \Delta^0 q(q) = -\Delta^0 q(q) \), which is to say that the internal flux is balanced by the flux from the reservoirs. In the intermediate regime, \( G(q, \tau) = g_0(q)/|\tau| \), and hence for small enough \( \tau \) one can neglect \( S_\omega(q) \), compared to \( G \). Also \( F(q, \tau) = f(q, \tau) \). Hence the first of these two results is \( \Delta^0 q = \tau g_0(q)^{-1} f(q, \tau) \), which is in agreement with the result for the isolated system, since \( X_r(q) = X_r \).

With these explicit expressions for the most likely transitions, the conditional total second entropy may be written as

\[
S^{(2)}(\Delta' q, \Delta^0 q | q, \tau, X_r) = \frac{1}{2} G(q, \tau) [\Delta^0 q - \Delta^0 q]^2 + \frac{1}{2} S_\omega(q) [\Delta^0 q - \Delta^0 q]^2 + \frac{1}{2} [\Delta^0 q - \Delta^0 q]^2 S_\omega(q)^{-1} [X_r - X_r(q)]^2 + \frac{1}{2} [G(q, \tau) - S_\omega(q)/2][\Delta^0 q - \Delta^0 q]^2.
\]

(103)

Here an immaterial constant dependent on \( q \) has been neglected. In view of the fact that this is a quadratic form in the two transitions and in view of the reduction condition upon integration over the two transitions, the unconditional total second entropy is

\[
S^{(2)}(\Delta' q, \Delta^0 q | \tau, X_r) = \frac{1}{2} G(q, \tau) [\Delta^0 q - \Delta^0 q]^2 + \frac{1}{2} S_\omega(q) [\Delta^0 q - \Delta^0 q]^2 + \frac{1}{2} [\Delta^0 q - \Delta^0 q] S_\omega(q) [\Delta^0 q - \Delta^0 q] + S^{(1)}(q) - q \cdot X_r.
\]

(104)

By construction, the derivative with respect to \( q \) evaluated at the optimum transitions is

\[
\frac{\partial S^{(2)}(\Delta' q, \Delta^0 q | q, \tau, X_r)}{\partial q} \bigg|_{\delta q, \Delta q} = X_r(q) - X_r,
\]

(105)

which evidently vanishes when the internal force equals the external force.

G. Phase space probability

In Refs. 5 and 7, the phase space probability distribution for a steady state system was given for variables of even parity. It consisted of two parts: the structural part, which was even in time and which was the analog of the usual equilibrium Boltzmann factor, and the so-called odd (or mirror or putative) work, which was odd in time and which represented the entropy cost to the reservoir of arriving at the current point in phase space.

One can take that result over directly to the present nonlinear, uneven case. In general one has for the steady state phase space probability distribution

\[
\rho(\Gamma|X_r) = \frac{1}{N h^{3N} Z_\omega(X_r)} e^{-q(q)|X_r|} e^{W^{odd}(\Gamma|X_r)}.
\]

(106)

Here \( Z_\omega \) is the normalizing partition function, whose logarithm gives the thermodynamic potential for the steady state, and the thermodynamic force applied by the reservoir is \( X_r \), which is constant even in the nonlinear regime of the subsystem. The odd work is

\[
W^{odd}(\Gamma|X_r) = \frac{1}{2} X_r \cdot [\hat{q}_0(\Gamma) - \hat{q}_0(\Gamma)]
\]

\[
= \frac{1}{2} \int_{-\tau}^{\tau} dt X_r \cdot \hat{q}(\Gamma_0(t|\Gamma))
\]

\[
= \frac{1}{2} \int_{-\tau}^{0} dt X_r \cdot \hat{q}(\Gamma_0(0|\Gamma)|\Gamma) - \hat{q}(\Gamma_0(0|\Gamma)|\Gamma))
\]

\[
\tau > 0,
\]

(107)

where \( \hat{q}_0(\Gamma) = \hat{q}(\Gamma_0(0|\Gamma)) \), and the subscript zero indicates the adiabatic trajectory (i.e., that of the isolated system). The integrand is related to the rate of production of first entropy of the reservoir and, as shown above, the time-dependent part of the second entropy force \( \mathcal{H}_1 \) does not contribute to this, which is why only the usual thermodynamic force of the reservoir, \( X_r \), appears in these expressions. As shown previously, \( S^{(2)}_\omega \) the odd work is independent of \( \tau \) for intermediate values of the time interval because the integrand asymptotes to its most likely value, which is odd in time. This result still holds for the present case of mixed parity because the second entropy force \( \mathcal{H}_1 \), which gives an even asymptote, does not contribute to this expression as it is orthogonal to
the reservoir force. Under the reversal of time, $\Gamma \rightarrow \Gamma^\dagger$ and $X_i \rightarrow e^X_i$, (magnetic fields and Coriolis forces have odd parity), the first or structural exponent is invariant, and the odd work or dynamic exponent changes sign. Finally, the nonlinear transport matrix $g_0(X_i)$ may be obtained from a steady state average of the fluctuations in the future position, and the second entropy force $f_i(X_i)$ may be obtained from the average steady state flux after subtracting the contribution due directly to the reservoir force.

III. CHEMICAL KINETICS

In this section the second entropy approach to nonequilibrium thermodynamics is applied to chemical kinetics. The aim is to illustrate some technical details of the application of the theory. In particular, the nonlinear regime is treated explicitly, since chemical reactions arguably represent the most common nonequilibrium system of a nonlinear nature.

Here a network of nonlinear reactions is characterized. The extent of reaction or reaction progressions are more useful variables to characterize the system than are the species number. The reaction rate matrix for the extent is diagonal, which has many numeric and analytic advantages. Denoting molecules of type $i$ by $a_i$, the system of reactions may be written as

$$\sum_i v_{ij} a_i = \sum_i \omega_{ij} a_i, \quad I = 1, 2, \ldots .$$  

The $v_{ij} \geq 0$ are the stoichiometric coefficients for reactants, which are zero if molecules of type $i$ are not a reactant in the $I$th reaction, and the $\omega_{ij} \geq 0$ are the stoichiometric coefficients for products, which are zero if molecules of type $i$ are not a product in the $I$th reaction. One defines $x_I$ as the progress or extent of reaction. The number of species $i$ changes with the progress of the reactions according to

$$dN_i = \sum_I (\omega_{ij} - v_{ij}) dx_I.$$  

Both $\mathbf{x}$ and $\mathbf{N}$ have odd parity, since reversing the molecular velocities instantaneously makes the reactions run in reverse at the same speed. Hence $\mathbf{x}$ and $\mathbf{N}$ have even parity. Some care has to be exercised in interpreting this remark, since not all phase points $\Gamma$ at time $t=\tau$ are compatible with the initial conditions $N_0$ at time $t=0$. However, if $\Gamma$ is compatible, then so is $\Gamma^\dagger$, and $\mathbf{x}(\Gamma^\dagger) = \mathbf{x}(\Gamma)$.

In classical chemical kinetics, the forward reaction rate is proportional to the product of powers of the concentrations of the reactants. Such an expression is obviously idealized and is most likely valid for a dilute gas. The order of the reaction is the sum of these powers. The powers are not necessarily integers, and they are not necessarily equal to the respective stoichiometric coefficients. However, in the case that the reaction represents a so-called elementary step, then the coefficients are the reactant stoichiometric coefficients. The reaction rate is the rate of progress, and in the present case of elementary reactions the classical theory says

$$\bar{x}_I(N) = k_I^+ \prod_i n_i^{\alpha_i} - k_I^- \prod_i n_i^{\beta_i} = k_I^+ R_I(N) - k_I^- P_I(N),$$  

where the concentrations are $N=N/V$.

For the second entropy approach, one requires the thermodynamic forces. If the reaction is carried out in the presence of a temperature and pressure reservoir, then the appropriate constrained free energy is related to the Gibbs free energy and is

$$G(x, E, V|N_0, p, T) = E + pV - TS(E, V, N).$$  

Optimizing this with respect to energy and volume, one obtains

$$G(x|N_0, p, T) = \bar{E} + p\bar{V} - TS(\bar{E}, \bar{V}, N).$$  

With this, the thermodynamic force conjugate to the extent is

$$X_I(N) = -\frac{1}{T} \frac{dG(x|N_0, p, T)}{dx_I}$$

$$= \sum_i \frac{\partial S(\bar{E}, \bar{V}, N)}{\partial N_i} \frac{\partial N_i}{\partial x_I}$$

$$= -\frac{1}{T} \sum_i (\omega_{ij} - v_{ij}) \mu_i(N).$$  

The right-hand side is essentially the so-called deDonder affinity. Here $\mu_i$ is the chemical potential of species $i$, which for the ideal case is $\mu_i = k_B T \ln(n_i/\bar{n}_i)$. The equilibrium condition is that the entropy should be a maximum with respect to further progress of the reactions, which is to say that the conjugate force should vanish. That is, $X_I(N) = 0$ or equivalently

$$\sum_i (\omega_{ij} - v_{ij}) \mu_i(N) = 0, \quad I = 1, 2, \ldots .$$  

The second entropy expression for the most likely rate of progress of the reactions in the intermediate regime is

$$\bar{x}_I(N) = -\frac{\text{sgn}(\tau)}{2} \frac{\partial g(N)}{\partial \bar{x}_I} X(N).$$  

(Because the extent of reactions has even parity, the driving forces that depend on $\bar{x}$ vanish, and hence the transport matrix is symmetric. To simplify the notation below, this is here written as $\bar{g}$ rather than as $g_\tau$.) The first result that one can obtain from this follows from the fact that at equilibrium the forces vanish, $X(N) = 0$. Hence one concludes that at equilibrium the individual reaction rates also vanish,

$$\bar{x}_I(N) = 0.$$  

This result is nontrivial and is the analog of detailed balance for a network of reactions. It means that the classical rate equation must satisfy $k_I^+ R_I(N) = k_I^- P_I(N)$, and hence the rate may be written as

$$\bar{x}_I(N) = k_I[R_I(N) - P_I(N)].$$  

The second result concerns the symmetry of a certain, almost traditional, rate coefficient matrix. The explicit expression for the rate of change of concentration is

\[ \dot{n}_i(n) = \frac{1}{V} \sum_j (\omega_{ij} - v_{ij}) \tilde{x}_j(n) \]

\[ = -\frac{\text{sgn}(\tau)}{2V} \sum_{i,j} (\omega_{ij} - v_{ij})(g^{-1})_{ij}X_j \]

\[ = \frac{\text{sgn}(\tau)}{2TV} \sum_{i,j} (\omega_{ij} - v_{ij})(g^{-1})_{ij}(\omega_{ij} - v_{ij})\mu_j \]

\[ = \sum_j \kappa_{ij}\mu_j. \quad (118) \]

Here

\[ \kappa_{ij} = \frac{\text{sgn}(\tau)}{2TV} \sum_{i,j} (\omega_{ij} - v_{ij})(g^{-1})_{ij}(\omega_{ij} - v_{ij}) = \kappa_{ji}, \quad (119) \]

since \( g \) is symmetric. Hence even for a network of nonlinear reactions, one can define a density-dependent rate matrix that gives the rate of change of concentration as a linear function of the thermodynamic forces, which need not be ideal, and this rate matrix is symmetric. This result has a direct interpretation in terms of macroscopic reversibility. No linearity of ideality has been assumed in this result.

The final result is the reduction of the present general, nonlinear, nonideal expression to the traditional expression. To do this one first asserts that the elementary reactions comprising the network are uncoupled in the sense that the progress of one does not directly influence the progress of the others. There is of course an indirect influence via the change in concentrations, but if there is no direct coupling, then the second entropy transport matrix is diagonal. Hence one has

\[ \tilde{x}_j(N) = -\frac{\text{sgn}(\tau)}{2g_{ij}(N)}X_j(N). \quad (120) \]

Now the thermodynamic force for an ideal gas is

\[ X_{ij}^0(N) = k_B \sum_i (v_{ij} - \omega_{ij})\ln \frac{n_i}{n_j} = k_B \ln \prod_i \left( \frac{n_i}{n_j} \right)^{v_{ij} - \omega_{ij}}. \quad (121) \]

Close to equilibrium, \( n_i \approx \bar{n}_i \), the logarithms may be linearized, which yields

\[ X_{ij}^{\text{lin}}(N) = k_B \left[ \ln \left( 1 + \prod_i \left( \frac{n_i}{n_j} \right)^{v_{ij}} - 1 \right) \right. \]

\[ - \ln \left( 1 + \prod_i \left( \frac{n_i}{n_j} \right)^{\omega_{ij}} - 1 \right) \]

\[ = k_B \left[ \prod_i \left( \frac{n_i}{n_j} \right)^{v_{ij}} - \prod_i \left( \frac{n_i}{n_j} \right)^{\omega_{ij}} \right]. \quad (122) \]

Evidently then, in this regime the present second entropy theory reduces to the classical reaction rate theory, and one has

\[ k_i = \frac{-k_B \text{sgn}(\tau)}{2g_{ii}} \quad (123) \]

and

\[ \kappa_{ij} = -\frac{1}{k_BTV} \sum_l k_l(\omega_{ij} - v_{ij})(\omega_{ij} - v_{ij}). \quad (124) \]

Comparing the second entropy expression [Eq. (120)] with the classical expression [Eq. (117)], one sees that in general they may be made equal by setting

\[ g_{ii}(n) = \frac{-X_i(n)/2}{k_i[R_i(m) - P_i(m)]} = \frac{-k_B \ln[R_i(m)/P_i(m)]}{2k_i[R_i(m) - P_i(m)]}, \quad (125) \]

where \( m_i = n_i/\bar{n}_j \). This is guaranteed correct near equilibrium, \( n = \bar{n} \), and it also provides a physically realistic limiting form as one or more of the concentrations vanish. With this the explicit expression for the second entropy in the intermediate regime is

\[ S^{(2)}(x', x|\tau) = S^{(1)}(n) + \frac{1}{2} \sum_i g_{ii}(n) \left( \dot{x}_i + \frac{\text{sgn}(\tau)X_i(n)}{2g_{ii}(n)} \right)^2 \]

\[ = S^{(1)}(n) - \frac{k_B |\dot{\tau}|}{4} \sum_i \ln[R_i(m)/P_i(m)] \]

\[ \times \left( \dot{x}_i - \frac{\text{sgn}(\tau)}{2}[R_i(m) - P_i(m)] \right)^2. \quad (126) \]

Here \( n = n_0 + V^\tau[\omega - \dot{v}]x \).

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