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Nonequilibrium thermodynamics for open systems

Hans Christian Öttinger*
Department of Materials, Polymer Physics, Eidgenössische Technische Hochschule Zürich, HCI H 543, CH-8093 Zürich, Switzerland

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We develop the general equation for the nonequilibrium reversible-irreversible coupling (GENERIC) framework of nonequilibrium thermodynamics for open systems. A clear distinction between bulk and boundary contributions to the Poisson and dissipative brackets employed to generate reversible and irreversible contributions to time evolution from energy and entropy allows us to formulate the bulk equations as well as the exchange and interaction with the environment directly. The full brackets keep all the structure and hence the predictive power of the original GENERIC for isolated systems. The straightforward procedure is illustrated for hydrodynamics of open systems. Boltzmann's kinetic equation is discussed as a further example. In the Appendix, the thermodynamic treatment of surface excess variables at walls and their role in boundary conditions for the bulk variables is exemplified for a diffusion cell.

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I. INTRODUCTION

The two-generator framework of nonequilibrium thermodynamics, in which the energy generates the reversible contribution to time evolution by means of a Poisson bracket and the entropy generates the irreversible contribution by a dissipative bracket [general equation for the nonequilibrium reversible-irreversible coupling (GENERIC)], was up to now developed only for isolated systems [1,2]. If one is interested in the bulk equations only, it has been argued on p. 8 of a recent textbook [3] that this is usually not a serious limitation: "Because we often deal with local field theories, the governing equations for which are independent of the boundary conditions, we should clearly be able to learn something about the thermodynamic admissibility of such evolution equations without paying any attention to the boundary conditions. For example, the field equations of hydrodynamics can be formulated without worrying about boundary conditions so that the difference between driven and isolated systems should not be important." If, however, one is explicitly interested in boundary effects or externally driven systems, the GENERIC framework must be extended. For a complete check of thermodynamic consistency, one should not just look at the evolution equations in the bulk, but also at the supplementing boundary conditions. The ultimate goal is a framework of coupled bulk and surface thermodynamics, anchored in statistical mechanics. Boundary conditions should arise naturally from physical insight and thermodynamic consistency, rather than by mathematical considerations and formal requirements.

The idea to develop boundary thermodynamics, which goes back to Waldmann [4], is supported by the fact that boundary conditions depend on the level of description chosen to represent the bulk properties of interest, and they are, hence, not unambiguous conditions at the boundary. This crucial difference between boundary conditions and conditions at the boundaries has been strongly emphasized in an inspiring paper by Brenner and Ganesan [5]. While the conditions existing at the boundary can be studied in any desired detail by laboratory or computer experiments, boundary conditions change their nature with the level of description, or with the coarse graining, and are, hence, intrinsically thermodynamic concepts. These abstract words are illustrated in the Appendix and in [5]. From a statistical mechanics perspective, a remarkable attempt to put boundary conditions for hydrodynamic equations on an equal footing with bulk transport processes has been made by Bocquet and Barrat [6].

Thermodynamic concepts are of key importance for the description of phenomena at surfaces and interfaces. In standard textbooks (see, for example, [7,8]), a surface contribution to the free energy appears to introduce surface tension and capillarity. A beyond-equilibrium thermodynamic framework for coupled bulk and interface phenomena will provide a backbone to the discussion of a variety of dynamic phenomena at surfaces and interfaces presented also in the above-mentioned textbooks, such as adsorption and/or desorption kinetics, spreading processes and spreading rates, evaporation rates, kinetics of nucleation, crystal growth, reactions in monolayers, and surface rheology of monolayers. For the special case of linear irreversible thermodynamics, the role of thermodynamics in describing interface transport processes and in providing boundary conditions for the bulk equations has been recognized early [4] and elaborated upon in detail [9–11].

In this paper, we offer a generalization of the GENERIC framework to open systems and we illustrate the abstract ideas for the example of hydrodynamics. As a further example, Boltzmann's kinetic equation is discussed briefly. Moreover, we explore the incorporation of surface excess variables for the example of a diffusion cell. Whereas attempts to generalize the GENERIC to driven systems by adding external, controllable, and observable variables within the framework of Dirac structures [12], and the comparison to the matrix model for driven systems [13,14] were made previously, we here focus on the boundary contributions to brackets for an unaltered list of variables in the spirit of Stokes-Dirac structures [15].

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*Electronic address: hco@mat.ethz.ch

II. BULK AND BOUNDARY CONTRIBUTIONS

As a reminder, within the GENERIC framework, the evolution of an arbitrary observable A is generated by the total system energy E and the entropy S according to

$$\frac{dA}{dt} = \{A,E\} + [A,S], \tag{1}$$

where abstract Poisson and dissipative bracket structures, $\{\cdot,\cdot\}$ and $[\cdot,\cdot]$, need to be introduced to generate reversible and irreversible contributions to the time evolution. These brackets possess a rich structure (see Sec. 1.2.1 of [3]), which expresses the predictive power of the GENERIC. In verifying the structure, boundary terms have always been neglected in a previous work. In the presence of boundary effects, Eq. (1) needs to be reconsidered carefully. In particular, we will realize how one should split the Poisson and dissipative brackets of the GENERIC into bulk and boundary contributions.

The bulk and boundary contributions to the brackets to be introduced below do not inherit the symmetry properties of the full brackets, and the bulk Poisson bracket does not possess the time-structure invariance property. It turns out that the full thermodynamic structure can only be recognized in the sum of the bulk and boundary contributions, which implies a strong coupling of bulk and boundary thermodynamics. Once the full Poisson and dissipative brackets are formulated, the formulation of bulk and boundary operators and the rest of the following construction are determined by straightforward recipes.

A. Poisson brackets

The Poisson brackets used to generate a reversible time evolution from an energy in the GENERIC [3] are characterized by the antisymmetry property

$$\{A,B\} = -\{B,A\}, \tag{2}$$

the product or Leibniz rule

$$\{AB,C\} = A\{B,C\} + B\{A,C\}, \tag{3}$$

and the Jacobi identity

$$\{A,\{B,C\}\} + \{B,\{C,A\}\} + \{C,\{A,B\}\} = 0, \tag{4}$$

where A, B, and C are arbitrary sufficiently regular real-valued functions or observables on a space of independent variables for a nonequilibrium system. These properties are well known from the Poisson brackets of classical mechanics, and they capture the essence of the mechanistically controlled reversible dynamics of physical observables, as determined by the first term on the right-hand side of Eq. (1).

For a system confined to a time-independent volume V with boundary ∂V, we next wish to split the full Poisson bracket with the properties (2)–(4) into bulk and boundary contributions,

$$\{A,B\} = \{A,B\}_{\text{bulk}} + \{A,B\}_{\text{boundary}}. \tag{5}$$

We assume that the independent variables are functions of position, $x=x(\boldsymbol{r})$ for $\boldsymbol{r} \in V$, and so are the functional derivatives $\delta A/\delta x(\boldsymbol{r})$. Fields as variables, together with local relationships between physical quantities, are clearly essential for a meaningful distinction between bulk and boundary effects. The bulk contribution to the Poisson bracket is expressed in the form

$$\{A,B\}_{\text{bulk}} = \left\langle \frac{\delta A}{\delta x}, \, L \cdot \frac{\delta B}{\delta x} \right\rangle, \tag{6}$$

where L is a linear differential operator and the standard scalar product between vector-valued functions $\boldsymbol{f}$ and $\boldsymbol{g}$ on V is used

$$\langle \boldsymbol{f},\boldsymbol{g} \rangle = \int_V \boldsymbol{f}(\boldsymbol{r}) \cdot \boldsymbol{g}(\boldsymbol{r}) d^3 r. \tag{7}$$

The motivation for writing bulk Poisson operators in the form (6) is given by the fact that it can be considered as a chain rule. The first factor in the scalar product expresses variations of the functional A due to changes in the fields x, and the second factor expresses changes of x, for example, with time. In general, the scalar product in Eq. (6) must hence be the same as the one employed in the definition of functional derivatives. In particular, the reversible contribution to the bulk time-evolution equations for the independent variables implied by Eq. (1) can now immediately be recognized as

$$\left(\frac{dx}{dt}\right)_{\text{rev}} = L \cdot \frac{\delta E}{\delta x}. \tag{8}$$

This observation is essential for the construction of Stokes-Dirac structures in [15], which couple bulk and boundary terms in a more general and abstract setting.

To investigate the symmetry properties of the bulk bracket in Eq. (6), we need to construct the adjoint of the operator L for the standard scalar product. Because the linear operator L is typically a first-order differential operator, the calculation of its adjoint involves integrations by parts, which leaves us with boundary terms spoiling the symmetry properties of the bulk bracket. These extra terms need to be incorporated into the boundary contribution to the Poisson bracket. We assume that the boundary Poisson bracket possesses the same general structure as the bulk Poisson bracket

$$\{A,B\}_{\text{boundary}} = \int_{\partial V} \frac{\delta A}{\delta x(\boldsymbol{r})} \cdot L^{\partial}(\boldsymbol{r}) \cdot \frac{\delta B}{\delta x(\boldsymbol{r})} d^2 r, \tag{9}$$

where the integration is over two-dimensional surface elements, and the boundary Poisson operator $L^{\partial}(\boldsymbol{r})$ accounts for the reversible exchange and interaction with the environment. The explicit forms of the bulk and boundary Poisson operators L and L^{∂} are obtained by rearranging a given Poisson bracket through integrations by parts. Usually, L is a first-order differential operator, so that L^{∂} is a matrix with regular functions as entries. Only the Poisson operator L associated with the bulk contribution to $\{A,B\}$ was considered in previous work for isolated systems because boundary terms were considered to be irrelevant.

Whereas the antisymmetry (2) and the Jacobi identity (4) are not inherited by the bulk and boundary contributions to the Poisson bracket, the definitions (6) and (9) of these bracket contributions in terms of functional derivatives imply the product or the Leibniz rule (3) for the individual contributions. The definitions (6) and (9) moreover imply that the invariance of the full Poisson bracket under changes of the independent variables is inherited by the individual contributions, with a corresponding natural transformation behavior of the operators L and L^{∂}.

An important further property of the Poisson bracket is the degeneracy of the total system entropy S, which is used to generate irreversible dynamics. It expresses the characteristic of entropy that it cannot be affected by any reversible dynamics. From many examples we know that, in the nomenclature of the present paper, this degeneracy is a property of the bulk contribution to the Poisson bracket that can be expressed as

$$L \cdot \frac{\delta S}{\delta x} = 0. \tag{10}$$

Note that there can be a reversible flux of entropy at the boundary so that we do not necessarily assume that a degeneracy requirement holds also for the boundary Poisson operator. Therefore, the entropy need not be a degenerate observable for the full Poisson bracket due to flow effects at the boundary. The full Poisson bracket, which possesses all the GENERIC structure, is equivalent to the pair (L, L^{∂}) of bulk and boundary Poisson operators.

B. Dissipative brackets

Dissipative brackets are used to construct the irreversible contribution to time evolution from the gradient of entropy according to the second term on the right-hand side of Eq. (1). They are characterized by the symmetry condition (for a more sophisticated discussion of symmetry properties of dissipative brackets see Sec. 3.2.1 of [3])

$$[A,B] = [B,A], \tag{11}$$

the product or the Leibniz rule

$$[AB,C] = A[B,C] + B[A,C], \tag{12}$$

and the non-negativeness condition

$$[A,A] \geqslant 0, \tag{13}$$

where A, B, and C are arbitrary sufficiently regular real-valued functions on the space of independent variables for a nonequilibrium system.

With the same motivation as Poisson brackets, dissipative brackets can also be split into bulk and boundary contributions

$$[A,B] = [A,B]_{\text{bulk}} + [A,B]_{\text{boundary}}. \tag{14}$$

The bulk contribution to the dissipative bracket is written as

$$[A,B]_{\text{bulk}} = \left\langle \frac{\delta A}{\delta x}, M \cdot \frac{\delta B}{\delta x} \right\rangle, \tag{15}$$

where M is a linear differential operator, sometimes referred to as a (bulk) friction operator.

To investigate the symmetry properties of the bulk bracket in Eq. (15), we need to construct the adjoint of the friction operator M for the standard scalar product. Because the linear operator M is typically a differential operator, calculation of its adjoint involves integrations by parts, so that M is not self-adjoint and $[A,B]_{\text{bulk}}$ is not symmetric because we are left with boundary terms. These terms need to be incorporated into the boundary contribution to the dissipative bracket, for which we assume the by now familiar structure

$$[A,B]_{\text{boundary}} = \int_{\partial V} \frac{\delta A}{\delta x(\boldsymbol{r})} \cdot M^{\partial}(\boldsymbol{r}) \cdot \frac{\delta B}{\delta x(\boldsymbol{r})} d^2 r, \tag{16}$$

where the boundary friction operator $M^{\partial}(\boldsymbol{r})$ accounts for a irreversible exchange and interaction with the environment. For transport processes, the bulk friction operator M is a second-order differential operator, so that the boundary friction operator M^{∂} is a first-order differential operator [because the rearrangement of the dissipative bracket in the form of Eq. (14) with the contributions (15) and (16) again involves integrations by parts].

As a generalization of Eq. (8), the complete bulk time-evolution equations for the independent variables can now be written as

$$\frac{dx}{dt} = L \cdot \frac{\delta E}{\delta x} + M \cdot \frac{\delta S}{\delta x}. \tag{17}$$

Whereas the symmetry (11) is not inherited by the bulk and boundary contributions to the Poisson bracket, the definitions (15) and (16) in terms of functional derivatives imply the product or Leibniz rule (12) for the individual contributions. The definitions (15) and (16) moreover imply that the invariance of the full dissipative bracket under changes of the independent variables is inherited by the individual contributions, with a corresponding natural transformation behavior of the operators M and M^{∂}.

The conservation of energy under irreversible dynamics is expressed by a well-established identity for the bulk friction operator

$$M \cdot \frac{\delta E}{\delta x} = 0. \tag{18}$$

In view of the possibility of an irreversible flux of energy at the boundary, we do not necessarily expect that a similar degeneracy requirement holds also for the boundary friction operator.

The full dissipative bracket is equivalent to the pair (M, M^{∂}) of bulk and boundary dissipative operators. Only the bulk operators L and M occur in the time-evolution equations and have been considered in a previous work for isolated systems; the operators L^{∂} and M^{∂} are related to the boundary conditions.

C. Conservation laws

To construct the time-evolution equations (17), we need only the bulk Poisson and friction operators L and M. By studying total balance equations, in a next step, we recognize the physical significance of the boundary Poisson and friction operators L^∂ and M^∂ accounting for exchange and interaction with the environment. Moreover, the significance of the full dissipative bracket is highlighted by looking at the total entropy production rate.

The rate of change of any observable A, which is a functional of the independent variables x in the volume V, is given by the scalar product of its functional derivative with the time derivative of x in Eq. (17), so that we have

$$\frac{dA}{dt} = \{A,E\}_{\text{bulk}} + [A,S]_{\text{bulk}}. \tag{19}$$

This time-evolution equation, which is the proper interpretation of Eq. (1) when attention is paid to boundary terms, can alternatively be expressed in terms of Poisson and dissipative operators acting on A rather than on the generators E and S,

$$\frac{dA}{dt} = \int_V \left(-\frac{\delta E}{\delta x} \cdot L + \frac{\delta S}{\delta x} \cdot M \right) \cdot \frac{\delta A}{\delta x} d^3 r + \int_{\partial V} \left[-\frac{\delta E}{\delta x} \cdot (L^\partial + L^{\partial T}) + \frac{\delta S}{\delta x} \cdot (M^\partial - M^{\partial T}) \right] \cdot \frac{\delta A}{\delta x} d^2 r. \tag{20}$$

From this equation, it is clear that only the symmetric part of L^∂ and the antisymmetric part of M^∂ play a role for the boundary terms. If, for example, M^∂ is a differential operator, then $(\delta S/\delta x) M^{\partial T}$ is defined by

$$\int_{\partial V} \frac{\delta S}{\delta x} \cdot M^{\partial T} \cdot \frac{\delta A}{\delta x} d^2 r = \int_{\partial V} \frac{\delta A}{\delta x} \cdot M^\partial \cdot \frac{\delta S}{\delta x} d^2 r. \tag{21}$$

In view of $\{E,E\}=0$ and the degeneracy requirements (10) and (18), the rate of change of the energy E and the entropy S can be rewritten as pure boundary terms

$$\frac{dE}{dt} = \int_{\partial V} \left[-\frac{\delta E}{\delta x} \cdot L^\partial + \frac{\delta S}{\delta x} \cdot (M^\partial - M^{\partial T}) \right] \cdot \frac{\delta E}{\delta x} d^2 r \tag{22}$$

for the conserved quantity E, and as a positive-semidefinite production term plus boundary terms for S,

$$\frac{dS}{dt} = [S,S] + \int_{\partial V} \left[-\frac{\delta E}{\delta x} \cdot (L^\partial + L^{\partial T}) - \frac{\delta S}{\delta x} \cdot M^\partial \right] \cdot \frac{\delta S}{\delta x} d^2 r. \tag{23}$$

These balance equations highlight the importance of the boundary Poisson and friction operators and the occurrence of the full dissipative bracket in the total entropy production.

The main result of this paper is that the full structure of the Poisson and dissipative brackets is reflected only partially in the Poisson and friction operators used in previous applications of the GENERIC to isolated systems. These bulk Poisson and friction operators determine the evolution equations (17) and (19) for bulk observables. The important extra information in the previously neglected boundary terms can be used to define boundary Poisson and friction operators. Their physical significance is most transparent in the boundary terms of the general evolution equation (20).

III. EXAMPLE: HYDRODYNAMICS

For our discussion of hydrodynamics, we use the mass, momentum, and internal energy density fields, $x=(\rho,\boldsymbol{M},\epsilon)$, as independent variables. We first give the total energy, entropy, and their gradients for reference, and then we specify the full Poisson and dissipative brackets to be decomposed into bulk and boundary contributions.

A. Energy and entropy

The total energy can naturally be obtained by adding the kinetic and internal energy densities and integrating the sum over the entire volume of the flowing system,

$$E = \int_V \left(\frac{\boldsymbol{M}^2}{2\rho} + \epsilon \right) d^3 r. \tag{24}$$

By taking functional derivatives with respect to the hydrodynamic fields we obtain

$$\frac{\delta E}{\delta x} = \begin{pmatrix} \frac{\delta}{\delta \rho} \\ \frac{\delta}{\delta \boldsymbol{M}} \\ \frac{\delta}{\delta \epsilon} \end{pmatrix} E(\rho,\boldsymbol{M},\epsilon) = \begin{pmatrix} -\frac{1}{2}\boldsymbol{v}^2 \\ \boldsymbol{v} \\ 1 \end{pmatrix}, \tag{25}$$

where the velocity field is given by $\boldsymbol{v}=\boldsymbol{M}/\rho$.

The explicit expression for the entropy is

$$S = \int_V s(\rho,\epsilon) d^3 r, \tag{26}$$

where the function $s(\rho,\epsilon)$ describes the equilibrium relationship between the densities of mass, internal energy, and entropy. Hydrodynamics is clearly based on the assumption of local equilibrium. By taking functional derivatives with respect to the hydrodynamic fields we obtain

$$\frac{\delta S}{\delta x} = \begin{pmatrix} \frac{\delta}{\delta \rho} \\ \frac{\delta}{\delta \boldsymbol{M}} \\ \frac{\delta}{\delta \epsilon} \end{pmatrix} S(\rho,\epsilon) = \begin{pmatrix} -\frac{\mu}{T} \\ 0 \\ \frac{1}{T} \end{pmatrix}, \tag{27}$$

where μ is the chemical potential per unit mass and T is the temperature of the local equilibrium system.

B. Poisson bracket

By transforming two frequently considered expressions for the Poisson bracket of hydrodynamics see [Eqs. (2.57) and (2.58) of [3]] from the entropy density to the internal energy density as an independent variable, we obtain

$$\begin{aligned}\{A,B\} = {}& \int_V \left[\frac{\delta B}{\delta\rho}\frac{\partial}{\partial \boldsymbol{r}}\cdot\left(\frac{\delta A}{\delta \boldsymbol{M}}\rho\right) - \frac{\delta A}{\delta\rho}\frac{\partial}{\partial \boldsymbol{r}}\cdot\left(\frac{\delta B}{\delta \boldsymbol{M}}\rho\right)\right] d^3r \\ & + \int_V \left[\frac{\delta B}{\delta \boldsymbol{M}}\frac{\partial}{\partial \boldsymbol{r}}:\left(\frac{\delta A}{\delta \boldsymbol{M}}\boldsymbol{M}\right) - \frac{\delta A}{\delta \boldsymbol{M}}\frac{\partial}{\partial \boldsymbol{r}}:\left(\frac{\delta B}{\delta \boldsymbol{M}}\boldsymbol{M}\right)\right] d^3r \\ & + \int_V \left[\frac{\delta B}{\delta\epsilon}\frac{\partial}{\partial \boldsymbol{r}}\cdot\left(\frac{\delta A}{\delta \boldsymbol{M}}\epsilon\right) - \frac{\delta A}{\delta\epsilon}\frac{\partial}{\partial \boldsymbol{r}}\cdot\left(\frac{\delta B}{\delta \boldsymbol{M}}\epsilon\right)\right] d^3r \\ & + \int_V p\left(\frac{\delta B}{\delta\epsilon}\frac{\partial}{\partial \boldsymbol{r}}\cdot\frac{\delta A}{\delta \boldsymbol{M}} - \frac{\delta A}{\delta\epsilon}\frac{\partial}{\partial \boldsymbol{r}}\cdot\frac{\delta B}{\delta \boldsymbol{M}}\right) d^3r \end{aligned} \tag{28}$$

and the alternative expression

$$\begin{aligned}\{A,B\} = {}& -\int_V \rho\left(\frac{\delta A}{\delta \boldsymbol{M}}\cdot\frac{\partial}{\partial \boldsymbol{r}}\frac{\delta B}{\delta\rho} - \frac{\delta B}{\delta \boldsymbol{M}}\cdot\frac{\partial}{\partial \boldsymbol{r}}\frac{\delta A}{\delta\rho}\right) d^3r \\ & - \int_V \boldsymbol{M}\cdot\left(\frac{\delta A}{\delta \boldsymbol{M}}\cdot\frac{\partial}{\partial \boldsymbol{r}}\frac{\delta B}{\delta \boldsymbol{M}} - \frac{\delta B}{\delta \boldsymbol{M}}\cdot\frac{\partial}{\partial \boldsymbol{r}}\frac{\delta A}{\delta \boldsymbol{M}}\right) d^3r \\ & - \int_V \epsilon\left(\frac{\delta A}{\delta \boldsymbol{M}}\cdot\frac{\partial}{\partial \boldsymbol{r}}\frac{\delta B}{\delta\epsilon} - \frac{\delta B}{\delta \boldsymbol{M}}\cdot\frac{\partial}{\partial \boldsymbol{r}}\frac{\delta A}{\delta\epsilon}\right) d^3r \\ & - \int_V \left[\frac{\delta A}{\delta \boldsymbol{M}}\cdot\frac{\partial}{\partial \boldsymbol{r}}\left(\frac{\delta B}{\delta\epsilon}p\right) - \frac{\delta B}{\delta \boldsymbol{M}}\cdot\frac{\partial}{\partial \boldsymbol{r}}\left(\frac{\delta A}{\delta\epsilon}p\right)\right] d^3r, \end{aligned} \tag{29}$$

which, after integrating each term by parts, differ only by boundary terms. When Beris and Edwards [16] derived the Poisson bracket for hydrodynamics from a variational principle of classical mechanics via a Lagrangian description of the fluid in Secs. 5.1–5.3 of their book, they arrived at the version in Eq. (28). The same Poisson bracket was also obtained from classical mechanics by means of the projection-operator method [17] (as can be verified by comparing the Poisson operator found in that paper to the one in Exercise 24 of [3]). Lie-Poisson reduction based on the group of space transformations and its natural action on scalar densities, however, suggests the form in Eq. (29) (see Secs. 3 and 4 of Appendix B in [3]; see also Eq. (9) of [18]). For isolated systems, boundary terms are irrelevant and the brackets in Eqs. (28) and (29) are equivalent. For open systems, it is important to identify the appropriate Poisson bracket with the correct boundary terms.

While both bracket expressions possess the defining antisymmetry property (2) and fulfill the Leibniz rule (3), the Jacobi identity (4) allows us to identify the correct form of the Poisson bracket. On the one hand, when the Jacobi identity is checked for the bracket in Eq. (29), no integrations by parts are needed, and no boundary terms arise (see Sec. 2.3.1 of [3]). The bracket in Eq. (29) strictly satisfies the Jacobi identity without any leftover boundary terms, as should actually be expected for a bracket constructed by the Lie-Poisson reduction. On the other hand, in the same calculation for the bracket in Eq. (28), leftover boundary terms do occur, for example, such as

$$\int_{\partial V}\left(\boldsymbol{M}\cdot\frac{\delta A}{\delta \boldsymbol{M}}\right)\left(\boldsymbol{n}\cdot\frac{\delta B}{\delta \boldsymbol{M}}\right)\left(\frac{\partial}{\partial \boldsymbol{r}}\cdot\frac{\delta C}{\delta \boldsymbol{M}}\right) d^2r, \tag{30}$$

which, in general, cannot be canceled by terms with permutations of A, B, and C. Here and in the following, $\boldsymbol{n}$ is the outwardly directed normal unit vector on the boundary. When the boundary conditions are such that the difference between Eqs. (28) and (29) vanishes, then also the leftover boundary terms in checking the Jacobi identity vanish. In general, however, Eq. (28) does not define a valid Poisson bracket.

We next construct the boundary Poisson operator associated with the valid full Poisson bracket (29). By performing the integrations by parts required to get $\delta A/\delta x$ free of any spatial derivatives as required by the expression (6) for the bulk Poisson operator, we obtain

$$L^{\partial} = \begin{pmatrix} 0 & \rho\boldsymbol{n} & 0 \\ 0 & \boldsymbol{M}\boldsymbol{n} & 0 \\ 0 & (\epsilon + p)\boldsymbol{n} & 0 \end{pmatrix}, \tag{31}$$

and the transposed operator

$$L^{\partial T} = \begin{pmatrix} 0 & 0 & 0 \\ \boldsymbol{n}\rho & \boldsymbol{n}\boldsymbol{M} & \boldsymbol{n}(\epsilon + p) \\ 0 & 0 & 0 \end{pmatrix}. \tag{32}$$

Note that we find an additional degeneracy requirement $L^{\partial}\delta S/\delta x = 0$ for the boundary Poisson operator in Eq. (31).

Only the sum of L^{∂} and $L^{\partial T}$ matters in the boundary terms of the time-evolution equation (20). For hydrodynamics we find

$$-\frac{\delta E}{\delta x}\cdot(L^{\partial} + L^{\partial T}) = -\boldsymbol{n}\cdot\begin{pmatrix} \boldsymbol{v}\rho \\ \rho\boldsymbol{v}\boldsymbol{v} + \left(\frac{1}{2}\rho\boldsymbol{v}^2 + \epsilon + p\right)\boldsymbol{1} \\ \boldsymbol{v}(\epsilon + p) \end{pmatrix}. \tag{33}$$

The normal component of the reversible mass flux is the physically expected one. The other entries in Eq. (33) are not the normal components of the proper physical fluxes of the conserved variables because the volume integral in Eq. (20) contains divergence terms that also contribute to the physical fluxes through the boundary.

C. Dissipative bracket

The dissipative bracket of conventional hydrodynamics contains contributions associated with the shear viscosity η, the bulk or dilatational viscosity κ, and the thermal conductivity λ^{q}; it is given by

$$[A,B] = \int_V \frac{\eta T}{2}\left[\frac{\partial}{\partial \boldsymbol{r}}\frac{\delta A}{\delta \boldsymbol{M}} + \left(\frac{\partial}{\partial \boldsymbol{r}}\frac{\delta A}{\delta \boldsymbol{M}}\right)^T - \dot{\boldsymbol{\gamma}}\frac{\delta A}{\delta \epsilon}\right] : \left[\frac{\partial}{\partial \boldsymbol{r}}\frac{\delta B}{\delta \boldsymbol{M}} + \left(\frac{\partial}{\partial \boldsymbol{r}}\frac{\delta B}{\delta \boldsymbol{M}}\right)^T - \dot{\boldsymbol{\gamma}}\frac{\delta B}{\delta \epsilon}\right] d^3r$$

$$+ \int_V \hat{\kappa} T \left[\frac{\partial}{\partial \boldsymbol{r}} \cdot \frac{\delta A}{\delta \boldsymbol{M}} - \frac{1}{2}\mathrm{tr}\, \dot{\boldsymbol{\gamma}} \frac{\delta A}{\delta \epsilon}\right]\left[\frac{\partial}{\partial \boldsymbol{r}} \cdot \frac{\delta B}{\delta \boldsymbol{M}} - \frac{1}{2}\mathrm{tr}\, \dot{\boldsymbol{\gamma}} \frac{\delta B}{\delta \epsilon}\right] d^3r + \int_V \lambda^{\mathrm{q}} T^2 \left[\frac{\partial}{\partial \boldsymbol{r}}\frac{\delta A}{\delta \epsilon}\right] \cdot \left[\frac{\partial}{\partial \boldsymbol{r}}\frac{\delta B}{\delta \epsilon}\right] d^3r, \tag{34}$$

where $\hat{\kappa} = \kappa - 2\eta/3$. The symmetry (11) is obvious by construction and the non-negativeness condition (13) is equivalent to non-negative transport coefficients. With this dissipative bracket and the gradient of entropy, we find the following total entropy production:

$$[S,S] = \int_V \left[\frac{\eta}{2T}\dot{\boldsymbol{\gamma}} : \dot{\boldsymbol{\gamma}} + \frac{\hat{\kappa}}{4T}(\mathrm{tr}\, \dot{\boldsymbol{\gamma}})^2 + \frac{\lambda^{\mathrm{q}}}{T^2}\left(\frac{\partial T}{\partial \boldsymbol{r}}\right)^2\right] d^3r. \tag{35}$$

After performing the required integrations by parts, we find the degeneracy (18) of the bulk dissipative operator for the energy gradient (25), and the boundary friction operator is identified as

$$M^{\partial} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \eta T\left[\boldsymbol{n} \cdot \frac{\partial}{\partial \boldsymbol{r}}\boldsymbol{1} + \left(\boldsymbol{n}\frac{\partial}{\partial \boldsymbol{r}}\right)^T\right] + \hat{\kappa} T \boldsymbol{n}\frac{\partial}{\partial \boldsymbol{r}} & -\eta T \dot{\boldsymbol{\gamma}} \cdot \boldsymbol{n} - \frac{1}{2}\hat{\kappa} T (\mathrm{tr}\, \dot{\boldsymbol{\gamma}})\boldsymbol{n} \\ 0 & 0 & \lambda^{\mathrm{q}} T^2 \boldsymbol{n} \cdot \frac{\partial}{\partial \boldsymbol{r}}, \end{pmatrix}, \tag{36}$$

which yields the separate degeneracy requirement $M^{\partial}\delta E/\delta x = 0$ for the boundary friction operator. Note that, like the total energy, the mass and momentum of the system are degenerate functionals of the dissipative bracket.

Only the difference of M^{∂} and $M^{\partial T}$ matters in the boundary terms of the general time-evolution equation (20). For hydrodynamics we find

$$\frac{\delta S}{\delta x}(M^{\partial} - M^{\partial T}) = -\boldsymbol{n} \cdot \begin{pmatrix} 0 \\ -\eta \dot{\boldsymbol{\gamma}} - \frac{1}{2}\hat{\kappa}\, \mathrm{tr}\, \dot{\boldsymbol{\gamma}} \boldsymbol{1} \\ -\lambda^{\mathrm{q}}\frac{\partial}{\partial \boldsymbol{r}}T \end{pmatrix}. \tag{37}$$

With Eqs. (33) and (37), the general time-evolution equation (20) leads to

$$\frac{dE}{dt} = -\int_{\partial V} \boldsymbol{n} \cdot \left[\left(\frac{1}{2}\rho \boldsymbol{v}^2 + \epsilon\right)\boldsymbol{v} + \boldsymbol{j}^{\mathrm{q}} + (p\boldsymbol{1} + \boldsymbol{\tau}) \cdot \boldsymbol{v}\right] d^2r, \tag{38}$$

and

$$\frac{dS}{dt} = [S,S] - \int_{\partial V} \frac{1}{T}\boldsymbol{n} \cdot [(\epsilon + p - \rho\mu)\boldsymbol{v} + \boldsymbol{j}^{\mathrm{q}}] d^2r, \tag{39}$$

where the heat flux $\boldsymbol{j}^{\mathrm{q}}$ is given by Fourier's law, $\boldsymbol{\tau}$ is Newton's expression for the stress tensor, the term $\epsilon + p - \rho\mu$ in Eq. (39) is given by Ts, and the total entropy production $[S,S]$ is given in Eq. (35). We thus recover the expected energy and entropy balance equations for hydrodynamics in open systems.

IV. EXAMPLE: BOLTZMANN'S KINETIC EQUATION

In Boltzmann's kinetic equation, the independent variable is the single-particle distribution function $f(\boldsymbol{r},\boldsymbol{p})$, where $\boldsymbol{r}$ and $\boldsymbol{p}$ are the position and momentum of a single particle in a rarefied gas. We here focus on the Poisson bracket because the dissipative bracket for Boltzmann's kinetic equation does not contain any spatial derivative operators. For such a strictly local dissipative collision mechanism, the boundary friction operator vanishes. All details on the GENERIC formulation of Boltzmann's kinetic equation can be found in Sec. 7.2 of [3].

A. Energy and entropy

In the absence of external forces, the total energy for a single-particle kinetic theory is given by the kinetic energy,

$$E[f] = \int_V d^3r \int d^3p \frac{\boldsymbol{p}^2}{2m} f(\boldsymbol{r},\boldsymbol{p}), \tag{40}$$

where m is the mass of the gas particles. The functional derivative of $E[f]$ is obtained to be

$$\frac{\delta E[f]}{\delta f(\boldsymbol{r},\boldsymbol{p})} = \frac{\boldsymbol{p}^2}{2m}. \tag{41}$$

Boltzmann's famous entropy expression is given by

$$S[f] = \int_V d^3r \int d^3p\, s(f(\boldsymbol{r},\boldsymbol{p}))$$

$$= -k_{\mathrm{B}} \int_V d^3r \int d^3p\, f(\boldsymbol{r},\boldsymbol{p}) \ln \frac{f(\boldsymbol{r},\boldsymbol{p})}{N}, \tag{42}$$

where $s(f)$ is the entropy density and N is the total number of gas particles. The proper functional derivative of $S[f]$ is given by (see Sec. 7.2.2 of [3])

$$\frac{\delta S[f]}{\delta f(\boldsymbol{r},\boldsymbol{p})} = - k_{\mathrm{B}} \ln \frac{f(\boldsymbol{r},\boldsymbol{p})}{N}. \tag{43}$$

B. Poisson bracket

As a consequence of the fact that the single-particle distribution function f is the only variable on the level of Boltzmann's equation, it is a simple exercise to verify that the expression

$$\{A,B\} = \int_V d^3r \int d^3p f\left[\left(\frac{\partial}{\partial \boldsymbol{r}}\frac{\delta A}{\delta f}\right)\cdot\left(\frac{\partial}{\partial \boldsymbol{p}}\frac{\delta B}{\delta f}\right) - \left(\frac{\partial}{\partial \boldsymbol{p}}\frac{\delta A}{\delta f}\right)\cdot\left(\frac{\partial}{\partial \boldsymbol{r}}\frac{\delta B}{\delta f}\right)\right] \tag{44}$$

defines a valid Poisson bracket. As for the energy and entropy, we have integrations over $\boldsymbol{p}$ in addition to those over $\boldsymbol{r}$. The corresponding bulk Poisson operator is obtained via integrations by part,

$$L = \frac{\partial}{\partial \boldsymbol{p}} \cdot f \frac{\partial}{\partial \boldsymbol{r}} - \frac{\partial}{\partial \boldsymbol{r}} \cdot f \frac{\partial}{\partial \boldsymbol{p}}. \tag{45}$$

The degeneracy requirement (10) follows from Eqs. (43) and (45) and the commutativity of partial derivatives, but the entropy S is not a degenerate function of the full bracket.

In order to formulate the total balance equations, we evaluate

$$-\frac{\delta E}{\delta x}\cdot(L^{\partial} + L^{\partial T}) = \boldsymbol{n}\cdot\frac{\boldsymbol{p}^2}{2m}\frac{\partial f}{\partial \boldsymbol{p}}. \tag{46}$$

Because L^{∂} can be symmetrized in Eq. (22), we obtain the following energy balance after integrating by parts:

$$\frac{dE}{dt} = -\int_{\partial V} d^2r \boldsymbol{n}\cdot\int d^3p \frac{\boldsymbol{p}}{m}\frac{\boldsymbol{p}^2}{2m} f. \tag{47}$$

From Eq. (23), we obtain the entropy balance

$$\frac{dS}{dt} = [S,S] + \int_{\partial V} d^2r\, \boldsymbol{n}\cdot\int d^3p \frac{\boldsymbol{p}^2}{2m}\frac{\partial f}{\partial \boldsymbol{p}}\frac{\partial s(f)}{\partial f} = [S,S] - \int_{\partial V} d^2r\, \boldsymbol{n}\cdot\int d^3p \frac{\boldsymbol{p}}{m} s(f). \tag{48}$$

The reversible boundary operator in Eq. (46) allows us to formulate the total energy and entropy balances associated with Boltzmann's kinetic equation in a convenient manner, and the surface terms in the resulting equations have obvious interpretations as kinetic energy and entropy fluxes.

V. PERSPECTIVES

The formulation of open systems by splitting the Poisson and dissipative brackets of the GENERIC framework of nonequilibrium thermodynamics into bulk and boundary contributions should be supported by statistical mechanics. The fact that previous attempts to derive the Poisson bracket of hydrodynamics from the canonical bracket of classical mechanics did not lead to the correct boundary terms suggests that, in the statistical approach, the boundary contributions on the atomistic level also somehow need to be taken into account in the coarse-graining procedure. The relationship between boundary conditions on different levels of description has been investigated in the work of Bocquet and Barrat [6,19], which offers a guideline to formulate statistical expressions for irreversible contributions to the boundary conditions based on the Green-Kubo formula and projection-operator technique that provide the statistical foundations of the GENERIC for bulk thermodynamics.

This paper offers a modest step toward a complete thermodynamic description of boundary physics beyond the regime of linear irreversible thermodynamics. In the situation considered here, the boundary contributions to the Poisson and dissipative brackets depend only on the bulk variables (and their derivatives) evaluated at the boundaries. In general, there will be additional variables at the boundaries, typically excess variables accounting for deviations from the bulk behavior near a boundary in a coarse-grained manner (as already introduced in Gibbs's pioneering work on interfaces; see, for example, Sec. III-5 of [8] or Sec. 3.6 of [20]). For example, momentum excess occurs for the slip of a fluid at a solid wall. An example with excess particles near the wall is discussed in the Appendix. For time-dependent boundaries, intrinsic or geometric characteristics of the boundaries may also necessitate additional boundary variables. Free boundaries often involve time dependence, and the example of sedimentation of a stabilized emulsion droplet with an inhomogeneous distribution of surfactant (see Example 5.6.1 of [20]), maybe even with viscoelastic interfacial rheological behavior, illustrates the richness of the interface phenomena for which a fully thermodynamic description is sought. All the boundary conditions required mathematically to obtain unique solutions of the bulk equations should arise naturally from a deeply rooted framework of boundary thermodynamics. This vision is substantiated by a simple example in the Appendix. The development of the general framework should be guided by linear irreversible thermodynamics, for which interfaces and boundary conditions have been discussed in great detail in several classical papers [4,9,10]. The generalization will be useful not only to describe highly nonlinear coupled bulk and interface transport processes, but also for including interfacial relaxation processes. If we go beyond transport processes, the structure is no longer provided by the form of local balance equations, so that there is a clear need for a general framework determining the structure of time-evolution equations.

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APPENDIX: EXAMPLE OF A DIFFUSION CELL

In this Appendix, we consider the three-dimensional version of a diffusion cell previously studied by Brenner and Ganesan [5]. A cubic diffusion cell of volume V (see Fig. 1) is filled with a dilute suspension of Brownian particles. The low solute particle number density in the bulk is given by $P(\boldsymbol{r})$. Two opposite sides of the diffusion cell are in contact with reservoirs maintaining concentrations P_1 and P_2 at these open boundaries of the cell. The other four sides are bounded by solid walls (W), at which there exists a surface excess area solute particle number density, $p(\boldsymbol{r})$.

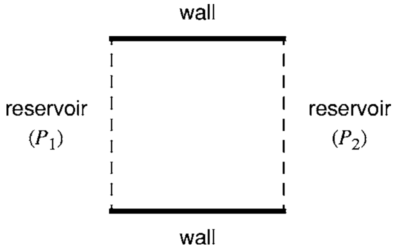

FIG. 1. Diffusion cell.

As we wish to describe purely isothermal diffusion of the Brownian particles in the cell filled with a quiescent viscous liquid and in the excess layers at the walls, we choose the GENERIC building blocks describing reversible dynamics to be zero, $E=0$ and $L=0$. For the entropy, we assume a sum of Boltzmann-type bulk and boundary contributions,

$$S = -k_{\mathrm{B}} \int_V P(\boldsymbol{r}) \ln P(\boldsymbol{r}) d^3 r - k_{\mathrm{B}} \int_W p(\boldsymbol{r}) \ln p(\boldsymbol{r}) d^2 r, \tag{A1}$$

and the derivatives of the entropy are thus given by

$$\frac{\delta S}{\delta P} = -k_{\mathrm{B}} \ln \frac{P}{P_0}, \tag{A2}$$

$$\frac{\delta S}{\delta p} = -k_{\mathrm{B}} \ln \frac{p}{p_0}. \tag{A3}$$

The constants P_0 and p_0, which are associated with normalization constraints of P and p in forming the functional derivatives, characterize the uniform distributions toward those P and p are driven by the entropy gradient.

Finally, the dissipative bracket includes three different irreversible mechanisms, namely, bulk diffusion, surface diffusion, and particle exchange between the bulk and the part of the surface bounded by walls,

$$\begin{aligned}[A,B] = {} & \frac{1}{k_{\mathrm{B}}} \int_V D_\infty \left[\frac{\partial}{\partial \boldsymbol{r}} \frac{\delta A}{\delta P(\boldsymbol{r})} \right] \cdot \left[\frac{\partial}{\partial \boldsymbol{r}} \frac{\delta B}{\delta P(\boldsymbol{r})} \right] P(\boldsymbol{r}) d^3 r \\ & + \frac{1}{k_{\mathrm{B}}} \int_W D_{\mathrm{s}} \left[\frac{\partial}{\partial \boldsymbol{r}} \frac{\delta A}{\delta p(\boldsymbol{r})} \right] \cdot \left[\frac{\partial}{\partial \boldsymbol{r}} \frac{\delta B}{\delta p(\boldsymbol{r})} \right] p(\boldsymbol{r}) d^2 r \\ & + \frac{1}{k_{\mathrm{B}}} \int_W \nu_{\mathrm{s}} \left(\frac{\delta A}{\delta p(\boldsymbol{r})} - \Omega \frac{\delta A}{\delta P(\boldsymbol{r})} \right) \\ & \times \left(\frac{\delta B}{\delta p(\boldsymbol{r})} - \Omega \frac{\delta B}{\delta P(\boldsymbol{r})} \right) p(\boldsymbol{r}) d^2 r. \end{aligned} \tag{A4}$$

In this bracket expression, D_∞ is the bulk diffusivity, D_{s} is the surface diffusivity, and ν_{s} is the rate at which adsorption to or desorption from the wall takes place (depending on the chemical potentials at the boundary and in the bulk). The factor Ω specifies the relationship between the surface excess variable and the bulk variable. In our simple example, where all particles moving from the bulk into a layer near the wall appear in the surface excess density, we have $\Omega=1$. We keep Ω as a reminder that, in general, one needs to establish a relationship between bulk and boundary variables, and that their dynamic coupling by dissipative processes contributes to the entropy production. All gradients $\partial / \partial \boldsymbol{r}$ of surface variables are understood as tangential derivatives along the surface.

In order to formulate the time-evolution equations implied by the above building blocks E, S, L, and the dissipative bracket (A4) for the bulk and surface excess variables, we rewrite the dissipative bracket as motivated above. The bulk contribution to the bracket involves only bulk variables

$$[A,B]_{\text{bulk}} = \left\langle \frac{\delta A}{\delta P}, M \frac{\delta B}{\delta P} \right\rangle, \tag{A5}$$

where M is the diffusion operator

$$M = -\frac{1}{k_{\mathrm{B}}} \frac{\partial}{\partial \boldsymbol{r}} \cdot D_\infty P \frac{\partial}{\partial \boldsymbol{r}}. \tag{A6}$$

For the boundary contribution we obtain after some integrations by parts and a splitting of the bulk-surface exchange term

$$\begin{aligned}[A,B]_{\text{boundary}} = {} & \int_{\partial V} \frac{\delta A}{\delta P(\boldsymbol{r})} M_1^{\partial}(\boldsymbol{r}) \frac{\delta B}{\delta P(\boldsymbol{r})} d^2 r \\ & + \int_W \frac{\delta A}{\delta p(\boldsymbol{r})} M_2^{\partial}(\boldsymbol{r}) \frac{\delta B}{\delta p(\boldsymbol{r})} d^2 r \\ & - \int_W \frac{\delta A}{\delta P(\boldsymbol{r})} \Omega^T M_B^{\partial}(\boldsymbol{r}) d^2 r + \int_W \frac{\delta A}{\delta p(\boldsymbol{r})} M_B^{\partial}(\boldsymbol{r}) d^2 r, \end{aligned} \tag{A7}$$

with

$$M_1^{\partial} = \frac{1}{k_{\mathrm{B}}} D_\infty P \boldsymbol{n} \cdot \frac{\partial}{\partial \boldsymbol{r}}, \tag{A8}$$

$$M_2^{\partial} = -\frac{1}{k_{\mathrm{B}}} \frac{\partial}{\partial \boldsymbol{r}} \cdot D_{\mathrm{s}} p \frac{\partial}{\partial \boldsymbol{r}}, \tag{A9}$$

$$M_B^\partial = \frac{\nu_s}{k_B}\left(\frac{\delta B}{\delta p} - \Omega\frac{\delta B}{\delta P}\right)p. \tag{A10}$$

Note that, in the construction of M_2^∂, we have neglected contributions from the edges of the diffusion cell. Treatment of these would require a lower-dimensional generalization of the present ideas, which seems to be a straightforward step (see also Chap. 18 of [20]).

As before, we identify the time-evolution equations for the bulk and boundary variables by the chain rule for the evolution of a general quantity A. In the bulk, we obtain the diffusion equation

$$\frac{dP}{dt} = M\frac{\delta S}{\delta P} = \frac{\partial}{\partial \boldsymbol{r}}\cdot D_\infty\frac{\partial P}{\partial \boldsymbol{r}}. \tag{A11}$$

For the open boundaries in contact with the reservoirs,

$$M_1^\partial\frac{\delta S}{\delta P} = \boldsymbol{n}\cdot\left(-D_\infty\frac{\partial P}{\partial \boldsymbol{r}}\right) \tag{A12}$$

gives the normal component of the particle flow through the surface of the diffusion cell. At the solid walls, there is no loss of particles, and an arbitrary quantity A can change only through changes of the surface excess variable p so that, by careful inspection of Eq. (A7) for $B=S$, we obtain the two requirements

$$M_1^\partial\frac{\delta S}{\delta P} = \Omega^T M_S^\partial \tag{A13}$$

and

$$\frac{dp}{dt} = M_2^\partial\frac{\delta S}{\delta p} + M_S^\partial, \tag{A14}$$

where $\Omega^T=\Omega=1$. In spite of these identities, we have kept the explicit factors of Ω and Ω^T to emphasize the two-way nature of the coupling between bulk and surface excess variables. The factor Ω^T in Eq. (A13) characterizes the influence of the surface excess variables on the boundary conditions for the bulk variables, whereas the factor Ω contained in M_S^∂ in Eq. (A14) describes the influence of the bulk behavior near the wall on the evolution of the surface excess variables.

The more explicit versions of Eqs. (A13) and (A14) for our diffusion cell are

$$\boldsymbol{n}\cdot\left(-D_\infty\frac{\partial P}{\partial \boldsymbol{r}}\right) = \nu_s p\ \ln\frac{Pp_0}{pP_0} = \nu_s p\ \ln\frac{HP}{p} \tag{A15}$$

with a characteristic length scale or boundary layer thickness $H=p_0/P_0$ (see Sec. III A of [5]), and the surface transport equation

$$\frac{dp}{dt} = \frac{\partial}{\partial \boldsymbol{r}}\cdot D_s\frac{\partial p}{\partial \boldsymbol{r}} + \boldsymbol{n}\cdot\left(-D_\infty\frac{\partial P}{\partial \boldsymbol{r}}\right). \tag{A16}$$

The coupled set of equations (A15) and (A16) determine the surface excess variable p and the boundary condition to the bulk variable P. This situation is more general than the one discussed in Sec. III D of [5] because we introduced a dissipative bracket contribution associated with the particle exchange between the bulk and the surface. This contribution is crucial for a full understanding of active transport in living cells [21]. Only if the exchange between the bulk and the surface happens very fast, the exchange term proportional to ν_s in the bracket (A4) can be neglected to obtain the results of [5]. The chemical potentials at the wall and in the bulk near the wall are then equalized for all times

$$\frac{\delta S}{\delta p} - \Omega\frac{\delta S}{\delta P} = 0 \quad \text{or} \quad p = HP. \tag{A17}$$

The condition $p=HP$ was used in Sec. III D of [5] together with the surface transport equation (A16) to fix the surface excess density and the boundary conditions. Equation (A15) then implies a vanishing normal flux to the wall, which is appropriate for the steady-state solution considered in detail in [5], but not for the suggested time-dependent generalizations. All the rich boundary physics of this diffusion cell is contained in the GENERIC building blocks.

A flavor of the statistical mechanics of the surface layer properties of the diffusion cell can be gained from the work of Brenner and Ganesan [5]. In that paper, the careful introduction of surface excess variables is based on a singular perturbation approach; the boundary layer thickness H is given in terms of the potential energy profile near the wall, and also an atomistic expression for the surface diffusivity is offered [see Eq. (78) of [5]). A thermodynamically consistent macroscopic description of polymer molecules near walls based on microscopic polymer models, including a calculation of slip coefficients, has been offered by Mavrantzas and Beris [22–24].

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