

# Reciprocity and cross coupling of two-phase flow in porous media from Onsager theory

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The symmetry properties of the permeability matrix in the macroscopic transport law for two-phase immiscible flow in porous media are investigated. The porous medium is treated as a single, closed thermodynamic system being forced by piston reservoirs. This construction is used to relate the Darcy fluxes to the time derivatives of the piston motion, and to identify the fluxes and forces in the Onsager sense. When the surface-tension forces that develop on the fluid interface are linear in the interface displacement, Onsager's theory is directly applicable and the permeability matrix must be symmetric. This argument is extended to show that reciprocity still holds when surfactants modify interface properties. [S1063-651X(99)08310-5]

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## I. INTRODUCTION

The linear Darcy laws governing two-phase flow in porous media have recently received broad attention—both theoretically [1–4] and experimentally [5–10]. These laws have the conventional form

$$J_i = \sum_j \frac{\kappa_{ij}(\phi)}{\eta_i} f_j, \quad (1)$$

where  $i$  and  $j$  label the phases and the fluid currents  $J_i$  are linked to the pressure gradients, or forces,  $f_i$ , via the permeabilities  $\kappa_{ij}$  and fluid viscosities  $\eta_i$ . Two main issues have been addressed in the literature: the range of validity of these linear Darcy equations and the question of whether the Onsager reciprocity relation  $\kappa_{ij}/\eta_i = \kappa_{ji}/\eta_j$  holds.

While continuum theory based on the Stokes equation [2,4] has been used to address these questions, it is of theoretical interest to show that Onsager theory [11–13] applies directly. This approach is also mathematically simpler than the techniques based on the continuum equations. As an example of this (relative) simplicity of application, we discuss the cases where the interfaces are allowed to move reversibly and where the interfaces have surfactants on them.

In order to apply Onsager theory [13], two theoretical components are needed. First, the entropy production in terms of the forces and fluxes (here  $f_i$  and  $J_i$ ) is needed. Second, the fluxes  $J_i$  must be identified as time derivatives of state variables characterizing the system on the level of coarse graining used. Being able to identify appropriate state variables is the crux of any application of Onsager's theorem. Here, this is accomplished by interpreting the driving pressures as forces that stem from external spring-piston devices.

The present paper complements the study in Ref. [4], which is based on the appropriate Stokes boundary-value problem. The theoretical approach is fundamentally different, but the main results are the same, save for the present application to the case where the fluid-fluid interface dynamics is complicated by the presence of surfactants.

## II. REVIEW OF ONSAGER'S THEORY

Before we consider the reciprocity associated with our specific problem in two-phase hydrodynamics, we first briefly review the basic requirements and results of the general Onsager theory [11,12]. A particularly clear and succinct review of the derivation has been given by de Groot [13]. In the simplest version, the theory deals with closed systems not far from equilibrium and described by a set of variables  $\{a_i\}$  that describes deviations from equilibrium. The theory addresses the symmetry properties of macroscopic linear transport laws having the form

$$J_i = L_{ij} X_j, \quad (2)$$

where  $X_i$  is a force that induces a current  $J_i$  and where the  $L_{ij}$ 's are constant coefficients. Summation over repeated indices is implied both here and throughout. When the indices refer to the fluid phases they take the values  $i=1,2$ . The force  $X_i$  is required to be conjugate to the current  $J_i$  in the sense that

$$X_i = \frac{\partial S}{\partial a_i} \quad \text{and} \quad J_i = \dot{a}_i, \quad (3)$$

where  $S = S(\{a_i\})$  is the entropy of the system. For the theory to apply,  $a_i$  must be small enough that the force is well approximated by  $X_i = (\partial^2 S / \partial a_i \partial a_j)_0 a_j$  where the 0 subscript denotes the equilibrium state in which  $a_i = 0$  for all  $i$ ; i.e., the theory requires the force to be linear in the state parameters  $a_i$ . The entropy production  $\dot{S}$ , which is positive in a closed system, takes the form

$$\dot{S} = \frac{\partial S}{\partial a_i} \dot{a}_i \equiv J_i X_i. \quad (4)$$

Thus, the definition of the appropriate currents and forces can also come from working out an analytical expression for the entropy production rather than determining the function  $S(\{a_i\})$  directly. Given these requirements on the currents and forces, the theory provides the fundamental result

$$L_{ij} = L_{ji}. \quad (5)$$

The remarkable aspect of the Onsager theory is that the result Eq. (5) is not based on any particular macroscopic property of the system, but is only a result of the time-reversal symmetry of the underlying microscopic equations of motion (Newton's laws or the Schrödinger equation). The laws of Eq. (2) may thus describe almost any kind of linear response that produces entropy.

We wish to emphasize the following point. The connection between microscopic dynamics and macroscopic transport is made through the so-called ‘‘Onsager regression hypothesis.’’ This states that *microscopic fluctuations in  $a_i$ , when averaged, decay in time according to the same laws, Eqs. (2), that control the macroscopic transport.* Onsager [11], deGroot [13], and others have traditionally presented this connection as an additional postulate of the theory. However, it is a simple exercise [14,15] to show that the regression hypothesis is generally valid whenever the external forces applied to the system are sufficiently small to warrant linear decay laws. The average in the statement of the regression hypothesis is an equilibrium ensemble average constrained so that the system is in a definite state at some definite initial time. The regression hypothesis is a fundamental law of linear-response theory equivalent to the fluctuation-dissipation theorem.

A useful fact easily proven is that any linear recombination of the forces and fluxes that leaves Eq. (4) invariant will also possess linear laws of the form Eq. (2) that satisfy Eq. (5). Moreover, the system may be described in any number of variables so long as Eq. (4) and Eq. (2) are fulfilled.

### III. THE FIXED-INTERFACE CASE

We begin with the simplest case where the interface between the two fluids is kept fixed since this will bring out the key parts of the argument and pave the way for the more realistic case where interface deformation is permitted. By ‘‘fixed interface’’ we mean simply that the interface retains its shape when force levels are changed; however, the fluid molecules attached to the interface will, in general, be moving along parallel with the interface. Physically this corresponds to assuming an infinite capillary number.

In order to describe a Darcy flow which is driven by external pressure gradients within the framework of the above theory, we have devised a system of springs and pistons as shown in Fig. 1. The purpose of this thought construction is to create a closed system for which the state variables  $\{a_i\}$  required by the Onsager theory are easily identifiable. The springs shown are assumed to have a long enough relaxation time for the system to remain close to a hydrodynamic steady state. For simplicity, the piston cross sections are taken to be equal to the cross section of the porous sample  $A$  so that

$$J_i = -\dot{a}_i \quad (6)$$

is precisely the volume of fluid  $i$  crossing unit area of the porous material in unit time where  $\dot{a}_i$  represents the rate of piston displacement. The minus sign arises because  $a_i$  is measuring distance to the piston from the piston position in

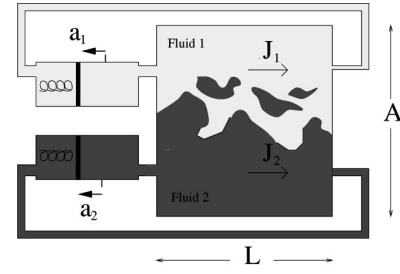


FIG. 1. Two fluid phases inside a sample of porous material of length  $L$  and cross-sectional area  $A$ . The porous material itself is not shown. The driving forces giving the external pressure gradients are represented by the springs acting on the pistons. The total piston-sample system is energetically and materially closed. The average macroscopic flux of each fluid is given by the time rate of change of the piston displacements  $a_1$  and  $a_2$ .

the totally relaxed state. It is also implicitly assumed that all resistance to flow comes from the porous material itself, which is equivalent to assuming that the ‘‘pipes’’ connecting the porous material to the piston chambers in this thought construction have large diameters.

We now determine an expression for the entropy production in the porous system, i.e., the system shown in Fig. 1 excluding the pistons and springs. This is a forced nonequilibrium system and the global Gibbs relation has the standard form

$$TdS \geq dE + dW, \quad (7)$$

where  $S$  is the entropy,  $E$  the internal energy of the fluids, and  $dW$  the work performed by the fluids. Being an inequality we cannot use this relation to determine the entropy production. In order to obtain this we shall need to employ the assumption of a *local* equilibrium and the corresponding local Gibbs relation [16]

$$Tds = d\varepsilon + p d\hat{v}, \quad (8)$$

where  $s$  and  $\varepsilon$  are the entropy and energy per unit mass while  $p$  is the pressure and  $\hat{v} = 1/\rho$  is the specific volume where  $\rho$  is the mass density. The conservation of mass can be written  $\rho d\hat{v}/dt = \nabla \cdot \mathbf{u}$  where  $\mathbf{u}$  is the local flow velocity and so the usual assumption of incompressible flow allows the pressure-work term to be neglected. Under such conditions,  $s$  is a function of  $\varepsilon$  alone so that

$$\frac{\partial s}{\partial t} = \frac{\partial s}{\partial \varepsilon} \frac{\partial \varepsilon}{\partial t} = \frac{1}{T} \frac{\partial \varepsilon}{\partial t}. \quad (9)$$

Because  $\rho$  is constant in time for incompressible flow, the entropy production can then be expressed

$$\begin{aligned} \frac{dS}{dt} &= \int dV \frac{\partial(\rho s)}{\partial t} = \int dV \frac{1}{T} \frac{\partial(\rho \varepsilon)}{\partial t} \approx \frac{1}{\bar{T}} \frac{dE}{dt} \\ &\quad - \int dV \frac{\Delta T}{\bar{T}^2} \frac{\partial(\rho \varepsilon)}{\partial t}, \end{aligned} \quad (10)$$

where the integration is taken over the entire system with the springs and pistons excluded and we have performed a Tay-

lor expansion in  $\Delta T = T - \bar{T}$ , where  $\bar{T}$  is the average temperature. The last term in Eq. (10) describes the entropy production caused by the internal heat flow in the system. (Writing the energy change  $\partial \rho \varepsilon / \partial t$  in terms of Fourier's law it can be shown to give a positive definite contribution to the entropy.)

Since it is of relative order  $\Delta T / \bar{T}$  compared to the  $dE/dt$  term it can be neglected whenever temperature variations are moderate. We have thus identified the condition under which Eq. (7) becomes an equality with  $dW=0$ . Note, however, that the total system (fluids plus pistons and springs) is *not* changing reversibly. In that case the entropy production would have been zero, which it is not. The system evolves through nonequilibrium states, and only the assumption of a local equilibrium allows the entropy to be computed.

The rate at which the springs perform work in moving the pistons is simply the product of the piston velocity  $-\dot{a}_i$  and the spring force  $k_s a_i$  where  $k_s$  is a spring constant. This power is simply  $dE/dt$ , the energy per unit time put into the porous sample. We assume that the inertial forces produced as the springs relax are negligible compared to the driving forces so that changes in kinetic energy are negligible compared to this spring power. The entropy production may then be written as

$$\frac{dS}{dt} = -k_s \frac{a_i \dot{a}_i}{\bar{T}}. \quad (11)$$

From this equation it may also be noted that a reversible change of the system, under which  $dS/dt=0$ , corresponds to the  $k_s \rightarrow 0$  limit. Thermodynamic forces  $X_i$  and fluxes  $J_i$  satisfying the requirements of Onsager's theory may be identified directly from Eq. (11) as

$$X_i = \frac{k_s}{\bar{T}} a_i \quad \text{and} \quad J_i = -\dot{a}_i. \quad (12)$$

Having made this observation we see that the general law Eq. (2) takes the specific form of the two-phase Darcy law Eq. (1) with the identification  $L_{ij} = \bar{T} \kappa \kappa_{ij} / (\eta_i AL)$  where the factor of  $\bar{T} / (AL)$  arises because  $f_i$  in Eq. (1) is the applied force per unit volume of porous material so that  $f_i = \bar{T} X_i / (AL)$ . Since the conditions for the Onsager theory have been met, we immediately can write

$$\frac{\kappa_{12}}{\eta_1} = \frac{\kappa_{21}}{\eta_2}, \quad (13)$$

which completes the proof that permeabilities are reciprocal in the fixed-interface case. Though we have appealed to a specific mechanical device (the pistons and springs), the reciprocity result obtained in this simple argument is perfectly general because our ideal devices are outside the system being treated. A comparison of the above three-line argument to the relatively more involved analysis based on Stokes's equation [4] demonstrates one of the great advantages in using Onsager's theorem.

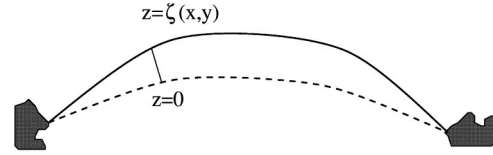


FIG. 2. The surface  $z = \zeta(x, y)$  represents the position of the fluid interface at any instant while the initial interface position is denoted by  $z=0$ . The coordinates  $x$  and  $y$  denote position along the initial interface.

#### IV. THE FLEXIBLE-INTERFACE CASE

We now consider the case when interfaces are free to change shape. For the Onsager theory to apply, the response must remain linear in the force. Thus, phenomena such as burstlike changes in the interface cannot be treated this way. What can be treated are small elastic deformations of the interface. In this case, the interface displacement is both linear and reversible in the applied force. In Ref. [4], a condition is given on the amount of local capillary-pressure variation that can be experienced before contact lines move. In what follows, we assume that such a condition is respected and that the interfaces (menisci) may stretch without significant movement of the contact lines.

Figure 2 shows an interface close to equilibrium, along with the variables by which the interface is described. The dashed line denotes the interface position  $z=0$  at zero forcing, while the solid line denotes the position  $z=\zeta$  after a normal displacement from equilibrium. The coordinates  $x$  and  $y$  lie along the interface.

In identifying the entropy production, the difference from the fixed-interface case is that now not only the pistons, but also the fluid interface will perform work on the fluids. By the *fluid interface* we always mean the layer of molecules which is affected by the presence of the molecules of the other fluid. By choosing to consider the interface together with the pistons as being external relative to the fluid bulk, we do not have to consider the internal entropy changes in the springs or the configurational entropy changes of the interface. Only the mechanical effect on the fluid bulk will be important, and the entropy production will, as before, be due to viscous heating in the fluids alone. We will take the same approach when studying interfaces with surfactants. The energy balance can thus be written

$$\bar{T} X_i J_i - dE_\zeta / dt = \bar{T} dS / dt, \quad (14)$$

where  $E_\zeta$  is the total surface energy of the interface. The left-hand side represents the energy put into the fluids per unit time due to the work of the pistons and interface while the right-hand side represents the manner in which the incompressibly flowing fluids store such energy; namely, as heat. As throughout the entire paper, viscous forces are assumed to dominate inertial forces so that changes in the kinetic energy are negligible relative to the heat production. The interface energy  $E_\zeta$  goes as

$$E_\zeta = \sigma A_\zeta, \quad (15)$$

where  $A_\zeta$  is the total interface area and  $\sigma$  is the surface tension [17]. The problem now is to characterize the changes

in interface area using variables that can be identified as state parameters  $\{a_i\}$  in the Onsager theory.

We now treat the special case where the interface is a plane before the springs begin to act (so that  $x$  and  $y$  are Cartesian coordinates). The analysis is particularly straightforward and instructive for this case. The general case where the initial interface is an arbitrarily curved surface is treated in the Appendix and gives similar results. Using a well-known expression for surface area, we have

$$A_\zeta = \int dx dy \sqrt{1 + (\nabla \zeta)^2} \quad (16)$$

$$\approx \int dx dy \left[ 1 + \frac{1}{2} (\nabla \zeta)^2 \right] \quad (17)$$

$$= A_{\zeta_0} \left( 1 + \frac{1}{2} \sum_{\mathbf{k}} \mathbf{k}^2 |\zeta_{\mathbf{k}}|^2 \right), \quad (18)$$

where  $\zeta = \zeta(x, y)$  represent the displacements from the initial plane  $z=0$  and where the integral is over the initial plane. In these expressions we have expanded the square root using the assumption of small deviations, switched to the finite Fourier transform  $\zeta_{\mathbf{k}} = A_{\zeta_0}^{-1} \int dx dy \exp(i\mathbf{k} \cdot \mathbf{x}) \zeta(\mathbf{x})$  where  $\mathbf{x} = (x, y)$  and  $\mathbf{k} = (k_x, k_y)$ , and applied Parseval's theorem. The constant  $A_{\zeta_0}$  is the initial interface area. The key step that allows Onsager theory to become applicable is the linearization of the square root which requires that  $(\nabla \zeta)^2 \ll 1$ ; i.e., only when the interface displacement remains much smaller than pore sizes will Onsager theory apply.

Upon taking the time derivative of Eq. (18) and using Eq. (15), Eq. (14) takes the form

$$\frac{dS}{dt} = X_i J_i + \sum_{\mathbf{k}} X_{\zeta \mathbf{k}} J_{\zeta \mathbf{k}}, \quad (19)$$

where the interface forces  $X_{\zeta \mathbf{k}}$  and fluxes  $J_{\zeta \mathbf{k}}$  are defined

$$X_{\zeta \mathbf{k}} = - \frac{\sigma A_{\zeta_0} \mathbf{k}^2}{\bar{T}} \zeta_{\mathbf{k}} \quad \text{and} \quad J_{\zeta \mathbf{k}} = \dot{\zeta}_{\mathbf{k}}. \quad (20)$$

Thus, for the special case of an initially flat interface, we have identified the appropriate state variables  $\zeta_{\mathbf{k}}$  required by the Onsager theory. The most general linear relationship between these fluxes and forces is then

$$\begin{pmatrix} \mathbf{J} \\ \mathbf{J}_\zeta \end{pmatrix} = \begin{pmatrix} \tilde{L} & M \\ M^T & Q \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{X}_\zeta \end{pmatrix}, \quad (21)$$

where the force vectors  $\mathbf{X}$  and  $\mathbf{X}_\zeta$  have components  $X_i$  and  $X_{\zeta \mathbf{k}}$ , respectively, and likewise for the current vectors  $\mathbf{J}$  and  $\mathbf{J}_\zeta$ . The matrix  $\tilde{L}$  is a  $2 \times 2$  permeability matrix controlling the flow when no interface forces act (zero surface tension) and is thus quite distinct from the fixed-interface permeabilities  $L$  of Sec. III that are defined when the surface tension is infinite. The matrix  $M$  has dimensions  $2 \times K$ , where  $K$  is the number of different wave numbers, while  $Q$  is a  $K \times K$  matrix. We have used Onsager reciprocity in writing  $M^T$  instead of some arbitrary  $K \times 2$  matrix. Onsager reciprocity also

gives that  $Q^T = Q$ . It is the matrices  $M$  and  $Q$  that properly allow for the presence of surface tension.

Combining the two equations in Eq. (21) by eliminating  $\mathbf{X}_\zeta$  allows the macroscopic flux to be expressed

$$\mathbf{J} = L\mathbf{X} + M Q^{-1} \mathbf{J}_\zeta, \quad \text{where} \quad L = \tilde{L} - M Q^{-1} M^T. \quad (22)$$

The coefficient matrix  $L$  controls the macroscopic flux when the interface has reached its steady-state position at which time  $\mathbf{J}_\zeta \equiv \dot{\zeta}_{\mathbf{k}} = \mathbf{0}$ . The steady-state matrix  $L$  can be identified as the fixed-interface matrix considered previously. The matrix  $\tilde{L}$  describes the unphysical case of fluid-fluid coupling in the *absence* of surface tension.

The only effect of the interface having moved a small distance to a new steady-state position is to change very slightly the relative permeabilities. Since such a slight change in permeability is proportional to  $\mathbf{X}$ , the effect of a steady-state interface displacement is to produce a quadratic force term in Darcy's law. Thus, in the purely linear laws considered here, the steady-state transport matrix  $L$  is the same as if the interface remained fixed.

We now make an order-of-magnitude estimate of the characteristic relaxation time required for the interface to reach its steady-state position. One can argue that while the interface is displacing with a speed  $\partial \zeta / \partial t$ , the viscous-shear stress  $\eta |\nabla \mathbf{u}| \approx \eta k \partial \zeta / \partial t$  produced by the associated flow will exactly balance the surface-tension forces  $\sigma k^2 \zeta$  driving the flow. Since dominant wave numbers  $k$  of the interface displacement will correspond to a characteristic pore dimension  $\ell_c$ , we can take  $k = 1/\ell_c$  and thus obtain a characteristic relaxation time  $t_c$  of

$$t_c = \ell_c \eta / \sigma. \quad (23)$$

For the typical range of values  $\ell_c \leq 10^{-4}$  m,  $\eta \leq 10^{-2}$  Pa s, and  $\sigma \geq 10^{-2}$  Pa m, we obtain that  $t_c \leq 10^{-4}$  s. In usual applications, the applied forces are varying over time scales considerably longer than  $t_c$ , in which case the steady-state laws  $\mathbf{J} = L\mathbf{X}$  are appropriate.

One may correctly object that even when no applied forces act, the fluid interface in the pores of a rock can never be characterized as being planar (this would violate the contact-line boundary condition that fixes the contact angle between the two fluids and the solid-grain surfaces). Thus, in the Appendix the more realistic case where interface displacements from an initially curved interface may occur is treated. Upon consulting the Appendix, it is seen that the results for an initially curved surface are similar to those when the interface is initially flat.

## V. COMPARISON WITH CASES OF LARGE INTERFACE DISPLACEMENTS

In the case of low saturation of nonwetting fluid, the linear Darcy laws may not be appropriate. As demonstrated by [3,18,19], the nonwetting phase may, at low concentrations, form bubbles that get stuck in the medium. The nonwetting phase is thus discontinuous and no flow of this phase is possible before the forcing is increased above some threshold  $X_c$  that allows the nonwetting phase to pass through the constricting pore throats. One might anticipate that when



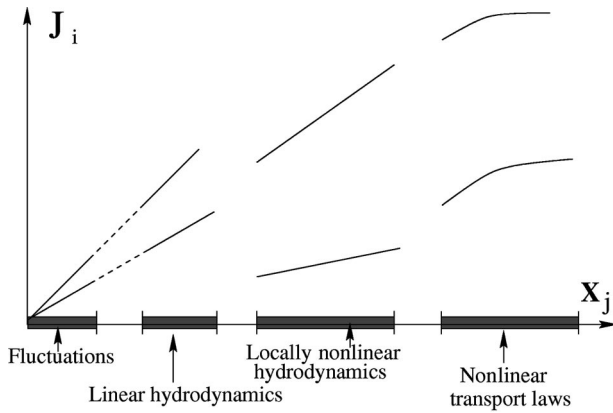


FIG. 3. Linear laws relating fluxes  $\mathbf{J}$  and forces  $\mathbf{X}$  showing how sufficiently large forces can, ultimately, violate the regression hypothesis.

$|X - X_c|$  is small, the flows could have a power-law dependence  $|X - X_c|^\nu$  with linear dependence only emerging as  $|X|$  becomes much larger than  $|X_c|$ . Although the simulations of [19] hint at such behavior, no firm justification can presently be given. Furthermore, when the nonwetting fluid is discontinuous, the pressure gradient it experiences cannot be independent from that on the wetting fluid. Hence, laws of the form Eq. (1), which are limited to the case where both phases continuously span the medium, are not in their most fundamental form. (In the simulations of Rothman, the macroscopic forces can be independently applied to each fluid regardless of the connectivity.)

As noted previously, Onsager's regression hypothesis is the key that allows the time-reversal symmetry of the molecular dynamics to be related to the macroscopic transport laws. For our case of piston reservoirs driving flow through a sample as depicted in Fig. 1, the regression hypothesis says that when the springs are totally relaxed and the system is in equilibrium, the spontaneous (thermally induced) fluctuation in either the piston position or the fluid-interface position will, on average, decay back to their equilibrium positions according to the macroscopic flow laws.

Due to their small magnitude, the average decay of fluctuations is described by linear hydrodynamics. Hence, the regression hypothesis can only link fluctuations and linear hydrodynamic flow on the macroscopic scale. Any nonlinearity in the description of the macroscopic flow will make the regression hypothesis useless. Figure 3 illustrates the different possible flow regimes. Only for the two regimes of the weakest force levels may the regression hypothesis be applied and theoretical statements on reciprocity made.

In the figure we allow for the possibility that even when something as locally nonlinear as a bubble breakup occurs, it is possible that the flow still might average to give linear macroscopic laws (at least approximately). However, because it is enormously improbable that bubble breakup occurs spontaneously from equilibrium fluctuations (such breakup arises when the flow is driven by externally compressed springs), there is no reason to expect the linear slope in such a macroscopic law to be the same as that corresponding to linear hydrodynamics and averaged fluctuations. Since nonreversible fluid redistributions driven by external spring forces can never be achieved through spontaneous fluctua-

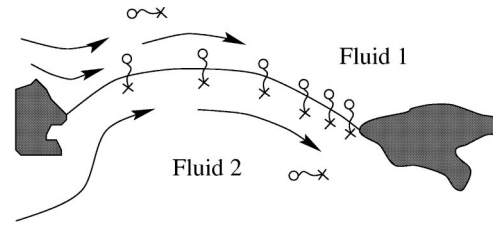


FIG. 4. A fluid interface with surfactants in a velocity field. The surfactant molecules have two ends, one that tends to be in fluid 1 ( $\circ$ ) and one that tends to be in fluid 2 ( $\times$ ).

tions, Onsager's theory only applies in situations of linear reversible interface deformation.

The numerical work of Olson and Rothman [19] shows that reciprocity holds to within the error of their simulations even when the macroscopic laws appear to be nonlinear. Under the circumstances this is rather remarkable. As shown here, Onsager theory can shed no light on such behavior.

## VI. SYMMETRY ACROSS COMPLEX INTERFACES: EFFECTS OF SURFACTANTS

In this section the Onsager theory is applied to interfaces with surfactants on them. In this case, the fluid flow will create spatial variations in the density of surfactants on the interface, and the surface tension, which depends on the surfactant density, will vary accordingly. This situation is illustrated in Fig. 4. The surface-tension gradients correspond to a tangential interface force that acts on the surrounding fluid in addition to the normal force due to the changes in surface curvature. The tangential forces will modify the interaction terms between the two fluids as described by the cross-coupling terms. While small interface displacements in the absence of surfactants left the steady-state viscous cross-coupling term  $L_{12}$  unchanged, the tangential forces due to gradients in surfactant density will modify  $L_{12}$ .

Writing down the energy contained in the surfactant gradients, and assuming the flow does not create gradients that go beyond linear approximations, it is possible to determine the mechanical effect of the interface surfactant gradients on the fluid bulk. It is then possible to follow the same lines as in the preceding section to show that reciprocity still holds in the presence of surfactants.

In order to do this, we first need to identify the surface energy associated with the gradients in the surfactant density. We start from the balance equation for the surface number density  $\Gamma_s$  of surfactant [20]

$$\frac{\partial \Gamma_s}{\partial t} + \nabla \cdot \mathbf{j}_s + j_n = 0. \quad (24)$$

The source term  $j_n$  represents the flow of surfactant onto and away from the interface. In order to identify the energy corresponding to a fixed amount of surfactant on the interface, we discard  $j_n$ . Hence the energy will correspond to the work the interface can do on the surrounding fluid during a time which is sufficiently short that the surfactant loss from the interface is negligible. We are left with the conservative version of Eq. (24). Further, the tangential force  $\mathbf{f}_s$  acting on a unit area of interface is simply the gradient in surface tension

$$\mathbf{f}_s = \nabla \sigma. \quad (25)$$

This force is related to the fluid stress tensor  $\mathbf{T}$  by the relation  $\mathbf{f}_s \cdot \mathbf{t} = \mathbf{n} \cdot [\mathbf{T}] \cdot \mathbf{t}$  where  $[\ ]$  denotes the difference across the interface and  $\mathbf{t}$  is an arbitrary tangent vector.

We will assume that the deviations from the equilibrium concentration  $\Gamma_0$  are small, i.e., that  $\Gamma_s = \Gamma_0 + \delta\Gamma_s$  where  $|\delta\Gamma_s| \ll \Gamma_0$ . This justifies the following linearizing approximations for the surface force and the surfactant velocity  $\mathbf{u}_s$ :

$$\mathbf{f}_s \approx \sigma'(\Gamma_0) \nabla \delta\Gamma_s, \quad (26)$$

$$\mathbf{u}_s \equiv \frac{\mathbf{j}_s}{\Gamma_s} \approx \frac{\mathbf{j}_s}{\Gamma_0},$$

where  $\sigma'(\Gamma_0) \equiv \partial\sigma/\partial\Gamma|_{\Gamma=\Gamma_0}$ . The velocity  $\mathbf{u}_s$  is the average velocity of the surfactant molecules relative to the solid matrix.

The surfactant energy associated with a  $\Gamma_s$  field is given as  $E_s = \int dW$  where the work  $dW$  is done in a relaxation process where  $\Gamma_s$  goes to a constant value. The work  $dW$  is done by the interface surfactant on the surrounding fluid on a small surface element  $dS$ . It can be written

$$dW = (\mathbf{f}_s dS) \cdot d\mathbf{x} = (\mathbf{f}_s dS) \cdot \mathbf{u}_s dt. \quad (27)$$

Using the approximations (26), the energy can be written

$$E_s = \int dW = \frac{\sigma'(\Gamma_0)}{\Gamma_0} \int dt \int dS \mathbf{j}_s \cdot \nabla \delta\Gamma_s. \quad (28)$$

Requiring the system to be materially closed (i.e.,  $\mathbf{j}_s = 0$  on the contact-line boundaries of the interface), a partial integration gives

$$E_s = - \frac{\sigma'(\Gamma_0)}{\Gamma_0} \int dt \int dS \delta\Gamma_s \nabla \cdot \mathbf{j}_s. \quad (29)$$

Equation (24) now gives

$$\begin{aligned} E_s &= \frac{\sigma'(\Gamma_0)}{\Gamma_0} \int dS \int dt \delta\Gamma_s \frac{\partial \delta\Gamma_s}{\partial t} = \frac{\sigma'(\Gamma_0)}{2\Gamma_0} \int dS \int dt \frac{\partial \delta\Gamma_s^2}{\partial t} \\ &= - \frac{\sigma'(\Gamma_0)}{2\Gamma_0} \int dS \delta\Gamma_s^2, \end{aligned} \quad (30)$$

where we have carried out the time integration assuming that  $\delta\Gamma_s$  decays from its initial value to zero. Switching to the spatial Fourier transform just as in Sec. IV, applying Parseval's theorem, and taking the time derivative, we get the rate of surfactant work

$$\dot{E}_s = - \frac{\sigma'(\Gamma_0) A \zeta_0}{\Gamma_0} \sum_{\mathbf{k}} \delta\Gamma_{s\mathbf{k}} \delta\dot{\Gamma}_{s\mathbf{k}}, \quad (31)$$

where, as before,  $\mathbf{k}$  is the wave number. The surfactant fluxes and forces may now be identified as

$$\mathbf{X}_\Gamma = - \frac{\sigma'(\Gamma_0) A \zeta_0}{\Gamma_0 \bar{T}} \delta\Gamma_s \quad \text{and} \quad \mathbf{J}_\Gamma = \delta\dot{\Gamma}_s. \quad (32)$$

Thus, the  $\delta\Gamma_s$  will serve as state variables in the Onsager theory. Since the force is linear in  $\delta\Gamma_s$  and since the flux is the time derivative of  $\delta\Gamma_s$ , the Onsager theory is applicable.

Allowing for interface displacement, there are now three separate mechanisms which will carry out work on the fluids. These are the springs, the relaxation of the interface, and the decay of surfactant gradients. The most general linear relations between the corresponding fluxes and forces now take the form

$$\begin{pmatrix} \mathbf{J} \\ \mathbf{J}_\zeta \\ \mathbf{J}_\Gamma \end{pmatrix} = \begin{pmatrix} \tilde{L} & M' \\ M'^T & Q' \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{X}_\zeta \\ \mathbf{X}_\Gamma \end{pmatrix}, \quad (33)$$

where the new matrixes  $M'$  and  $Q'$  play the same role as in Eq. (21), but where they now include the effect of the surfactants.  $M'$  and  $Q'$  act on the couple  $(\mathbf{X}_\zeta, \mathbf{X}_\Gamma)^T$ . As before the  $2 \times 2$  matrix  $\tilde{L}$  acts only on  $\mathbf{X}$ . Assuming a steady state, so that

$$\begin{pmatrix} \mathbf{J}_\zeta \\ \mathbf{J}_\Gamma \end{pmatrix} = \mathbf{0} \quad (34)$$

we can proceed exactly as in Sec. IV to eliminate the forces  $\mathbf{X}_\zeta$  and  $\mathbf{X}_\Gamma$  to get

$$\mathbf{J} = L' \mathbf{X}, \quad \text{where} \quad L' = \tilde{L} - M' Q'^{-1} M'^T. \quad (35)$$

Now, since the Onsager theory ensures the  $Q'^T = Q'$ , we get the final result

$$L' = L'^T. \quad (36)$$

By this we have shown that within the regime of linear response, reciprocity holds even when surfactant concentration gradients cause tangential interface forces to act on the fluid interface. We note as well that from a different perspective, one could define the changes in surfactant work as the product of the surfactant chemical potential  $\mu_s$  with local changes in the surfactant number densities along the interface. The equivalence of this definition with the one given above is due to the thermodynamic relation  $d\sigma = -\Gamma_s d\mu_s$  that relates changes in chemical potential to changes in surface tension  $\sigma$  for single-surfactant isothermal systems [21].

In showing the result (36) Onsager theory has proved quite convenient. However, the result could also have been obtained by means of the hydrodynamic equations. The Onsager analysis is limited to cases where deviations in the surfactant concentrations are sufficiently small that the response is linear in the applied force. Boghosian *et al.* [22] have recently introduced cellular automata models that include hydrodynamics, surface tension, and surfactants. Such models may provide efficient means to empirically investigate the regimes of nonlinearity for which the present analysis remains silent.

## VII. CONCLUSIONS

We have demonstrated that the Darcy laws given in Eq. (2) satisfy reciprocity up to linear order in the external forces. The domain of the linear laws is limited by the lin-

earity of the interface deformation. Hence dynamic saturation dependence, as is often the case in practical applications, violates linearity in a strict sense. It is observed, however, that apparently linear flux force relations hold well beyond what would be expected from these considerations [3,18,19]. In order to bridge the gap between the present results and those of irreversible fluid front motion, further experimental or numerical effort is needed [23,24].

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**APPENDIX: TRANSPORT LAWS**

**WHEN THE INITIAL FLUID INTERFACE IS CURVED**

In this appendix, we use the Onsager theory to establish the transport laws for the general case where the initial (zero force) fluid interface is curved. A system of ‘‘normal coordinates’’  $(x,y,z)$  is introduced in which  $x$  and  $y$  are still orthogonal but are now curvilinear coordinates tangent to the curved initial interface and possessing metrical coefficients (units of inverse length)  $h_x=h_x(x,y,z)$  and  $h_y=h_y(x,y,z)$ . The coordinate  $z$  measures distance normal from the initial interface position and thus has a metrical coefficient  $h_z=1$ . Surface properties associated with these coordinates are defined in Ref. [4].

It is easy to show [25] that the rate at which the interface area is changing is given as

$$\frac{dA_\zeta}{dt} = \int \frac{dx dy}{h_x h_y} (H - H_0) \frac{d\zeta}{dt}, \tag{A1}$$

where  $H=H(x,y,t)$  is the mean curvature (the sum of the two eigencurvatures) at each point on the surface  $z=\zeta$  while  $H_0$  is the mean curvature of the initial interface  $z=0$ . The integral is over the initial surface. In Ref. [4] it is shown that when the displacements  $\zeta$  are small compared to the initial curvature so that only terms linear in  $\zeta$  are retained in  $H$ , then

$$H = H_0 - (\nabla^2 \zeta + \xi^2 \zeta), \tag{A2}$$

where both the coefficient  $\xi(x,y)$  and the initial curvature  $H_0(x,y)$  are defined entirely by the metrical coefficients as given in Ref. [4]. The linearization of  $H$  is the key step that allows Onsager theory to become applicable.

The first law then takes the form

$$\frac{dS}{dt} = X_i J_i + \frac{\sigma}{\bar{T}} \int \frac{dx dy}{h_x h_y} [\nabla^2 \zeta + \xi^2 \zeta] \frac{d\zeta}{dt}. \tag{A3}$$

Thus, for each element  $(x+dx,y+dy)$  of the surface  $z=0$ , we can identify an interface force  $X_\zeta(x,y)$  and an interface flux  $J_\zeta(x,y)$  as

$$X_\zeta = \frac{\sigma}{\bar{T}} [\nabla^2 \zeta + \xi^2 \zeta] \quad \text{and} \quad J_\zeta = \dot{\zeta}. \tag{A4}$$

As required by the Onsager theory, the interface force is linear in the state parameters  $\zeta(x,y)$  while the interface flux is the time derivative of the state parameter. Thus, the proper fluxes and forces to be used in the transport laws have been identified.

The Onsager theory can now be used to write the linear transport laws in the form

$$\begin{aligned} J_1 &= \tilde{L}_{11} X_1 + \tilde{L}_{12} X_2 + \int M_1(x,y) X_\zeta(x,y) \frac{dx dy}{h_x h_y}, \\ J_2 &= \tilde{L}_{21} X_1 + \tilde{L}_{22} X_2 + \int M_2(x,y) X_\zeta(x,y) \frac{dx dy}{h_x h_y}, \\ J_\zeta(x,y) &= M_1(x,y) X_1 + M_2(x,y) X_2 \\ &\quad + \int Q(x,y|x',y') X_\zeta(x',y') \frac{dx' dy'}{h_{x'} h_{y'}}, \end{aligned} \tag{A5}$$

where the theory also provides the symmetry

$$Q(x,y|x',y') = Q(x',y'|x,y). \tag{A6}$$

An inverse kernel  $Q^{-1}$  is defined by the operation

$$\begin{aligned} \delta(x-x',y-y') &= \int Q^{-1}(x,y|x'',y'') Q(x'',y''|x',y') \\ &\quad \times \frac{dx'' dy''}{h_{x''} h_{y''}}, \end{aligned} \tag{A7}$$

with  $\delta$  being the Dirac delta. Thus, if Eq. (A5) is multiplied by  $Q^{-1}$  and integrated over  $z=0$ , the interface force  $X_\zeta$  can be identified as

$$\begin{aligned} X_\zeta(x,y) &= X_1 \int Q^{-1}(x,y|x',y') M_1(x',y') \frac{dx' dy'}{h_{x'} h_{y'}} \\ &\quad + X_2 \int Q^{-1}(x,y|x',y') M_2(x',y') \frac{dx' dy'}{h_{x'} h_{y'}} \\ &\quad + \int Q^{-1}(x,y|x',y') J_\zeta(x',y') \frac{dx' dy'}{h_{x'} h_{y'}}. \end{aligned} \tag{A8}$$

In principle, one could solve for  $\zeta(x,y,t)$  using Eq. (A5) for  $J_\zeta = \partial\zeta/\partial t$ . If the resulting linear expression in  $X_1$  and  $X_2$  is inserted into Eq. (A8),  $X_\zeta$  can be entirely eliminated from the laws for  $J_1$  and  $J_2$ . In the steady-state limit where  $J_\zeta \equiv \dot{\zeta} = 0$  (i.e.,  $t \gg t_c$ ), this task is made trivial and the transport laws become

$$\begin{pmatrix} J_1 \\ J_2 \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} \\ L_{12} & L_{22} \end{pmatrix} \begin{pmatrix} X_1 \\ X_2 \end{pmatrix}, \tag{A9}$$

where the steady-state transport coefficients are defined

$$L_{11} = \tilde{L}_{11} - \int \frac{dx dy}{h_x h_y} \int \frac{dx' dy'}{h_x h_y} \times M_1(x, y) Q^{-1}(x, y | x', y') M_1(x', y'), \quad (\text{A10})$$

$$L_{12} = \tilde{L}_{12} - \int \frac{dx dy}{h_x h_y} \int \frac{dx' dy'}{h_x h_y} \times M_1(x, y) Q^{-1}(x, y | x', y') M_2(x', y'), \quad (\text{A11})$$

$$L_{22} = \tilde{L}_{22} - \int \frac{dx dy}{h_x h_y} \int \frac{dx' dy'}{h_x h_y} M_2(x, y) Q^{-1}(x, y | x', y') \times M_2(x', y'). \quad (\text{A12})$$

Thus, so long as the interface displacement remains small relative to pore sizes, reciprocity is seen to hold.

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