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Pressure and relative motion in colloidal suspensions

S. S. L. Peppin
Department of Applied Mathematics and Theoretical Physics, University of Cambridge, Cambridge CB3 0WA, United Kingdom and Department of Chemical and Materials Engineering, University of Alberta, Alberta T6G 2G6, Canada

J. A. W. Elliott
Department of Chemical and Materials Engineering, University of Alberta, Alberta T6G 2G6, Canada

M. G. Worster
Department of Applied Mathematics and Theoretical Physics, University of Cambridge, Cambridge CB3 0WA, United Kingdom

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We examine the nature of relative motion in colloidal suspensions. By distinguishing carefully between the thermodynamic pressure of a mixture, defined by Gibbs, and the pressure measured by Darcy in porous media, we resolve apparent contradictions between the results and interpretations of different experiments. We show that Fick's and Darcy's laws, two empirical equations thought to describe different and complementary physical phenomena, are in fact particular limits of a single, unifying thermodynamic equation which can be used more generally to describe transport in colloidal systems. Importantly, this equation relates macroscopically measurable quantities. We use it to provide new interpretations of experiments in ultrafiltration. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1915027]

I. INTRODUCTION

The pressure distribution in two-component systems undergoing relative motion, such as the motion occurring during ultrafiltration (Sec. III), has been a fascinating subject of debate for some time. One early work[1] indicated that the pressure distribution must be accounted for to describe the mass flux in ultrafiltration boundary layers while later authors[2–4] claimed the pressure was constant. One experiment[5] measured a constant pressure throughout such a layer, while another[6] reports a significant pressure variation. In the following sections, we show that this controversy can be resolved by distinguishing carefully between the various pressures used to describe such systems. An interesting consequence of this work is a proof that several of the relations used to model relative motion of two species (including Fick's law, Darcy's law, and the modified Darcy's law) are equivalent.

II. FICK'S AND DARCY'S LAWS

While studying the diffusion of a dilute aqueous suspension of salt ions in a closed container, Fick proposed that the motion could be described by a linear relation between the flux of mass and the concentration gradient.[7] The modern form of Fick's law is given by the expression[8,9]

$$\mathbf{J}_2^0 = -D\,\boldsymbol{\nabla}\,\rho_2, \tag{1}$$

where $\mathbf{J}_2^0=\rho_2(\mathbf{v}_2-\mathbf{v}^0)$ is the mass flux of the ions relative to the volume average velocity, ρ_2 is the partial mass density of the salt ions, $\mathbf{v}_2$ is the local average velocity of the ions, and D is the diffusion coefficient. The volume average velocity is

$$\mathbf{v}^0 = \rho_1\nu_1\mathbf{v}_1 + \rho_2\nu_2\mathbf{v}_2 = (1-\phi)\mathbf{v}_1 + \phi\mathbf{v}_2, \tag{2}$$

where ν_2 is the partial specific volume and $\phi=\rho_2\nu_2$ the volume fraction, of component 2.

A year later, Darcy published his observations on the movement of water through a saturated column of sand.[10] In Darcy's experiment he first allowed a suspension of silica particles to sediment to the bottom of his apparatus (Fig. 1). He then allowed water to permeate through the sedimented particles and measured the fluid pressure using manometers such as those in Fig. 1. It was found that the motion could be correlated by a linear relation between the volume flux of water and the drop in pressure. The modern form of Darcy's law is[11]

$$\mathbf{q} = -\frac{k}{\eta}(\boldsymbol{\nabla} p - \rho_f\mathbf{g}), \tag{3}$$

where $\mathbf{q}=(1-\phi)(\mathbf{v}_1-\mathbf{v}_2)$ is the volume flux of permeating fluid relative to the particles, k is the permeability, η is the viscosity of the fluid, p is a pressure which we define carefully in Sec. IV, ρ_f is the density of the fluid, and g is the acceleration due to gravity. Fick's and Darcy's equations were based on experimental evidence, and their range of validity is not known.

III. ULTRAFILTRATION

Ultrafiltration is a separation process in which a colloidal solution[12] is forced against a membrane or partition that allows the solvent to pass through while retaining the colloids on the high-pressure side. As the particles build up against the membrane they form a concentrated boundary layer (Fig. 2). Such boundary layers also occur in reverse osmosis,

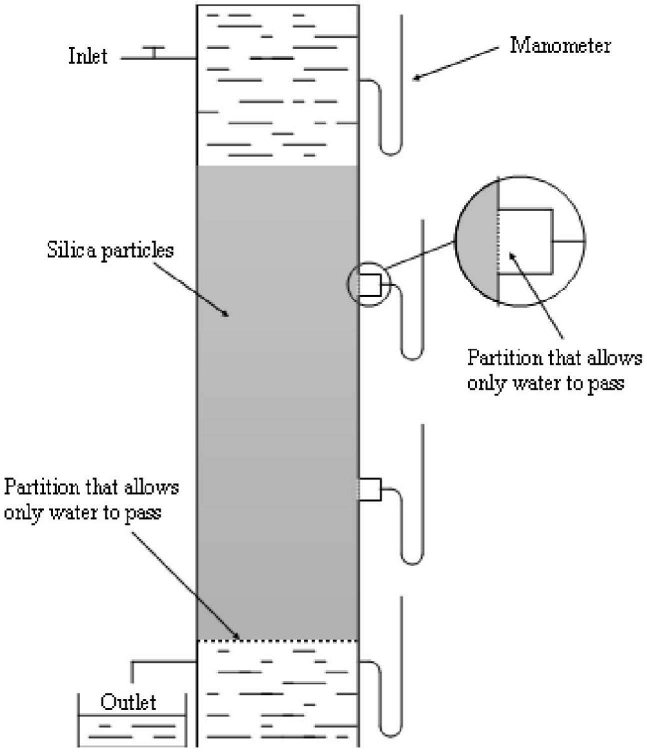

FIG. 1. Device used by Darcy in his study of permeation (Ref. 10). He first allowed a suspension of silica particles to settle to the partition. He then allowed water to pass through the system and measured the drop in pressure of the fluid in the manometers.

where the solutes being filtered are usually salt ions, and in mechanical filtration, where the solutes are particles of much larger size. Although the basic phenomenon occurring in all such boundary layers is essentially the same—one component of a binary mixture builds up against the partition while the other passes through—very different conceptual models have been used in the past to study reverse osmosis, ultrafiltration, and ordinary filtration.

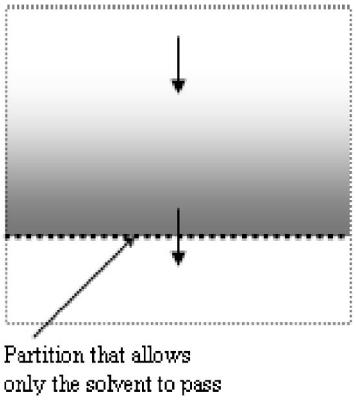

FIG. 2. Schematic of a filtration boundary layer (sometimes referred to as an unstirred layer, a concentration polarization layer, or a filter cake). The gray region is a binary mixture. The white regions represent pure component 1, the solvent or permeate. Component 2 can be a solution component (reverse osmosis), suspended colloids or macromolecules (ultrafiltration), or a porous matrix (mechanical filtration). The sides of the flow cell are assumed frictionless or far enough away to have no effect on the filtration process.

In reverse osmosis the layer is treated as a region undergoing molecular diffusion;[13] the constitutive relation used to describe the flux of solute within the layer is Fick's law. Conversely, in mechanical filtration, where the solute particles are very large (relative to the particle size in reverse osmosis), the layer is treated as a porous medium;[14] the constitutive relation used to describe relative motion within the layer is Darcy's law. In ultrafiltration, the solute particles are intermediate in size, and there is uncertainty in the literature concerning the appropriate constitutive relation to use in this case. The traditional conceptual picture of ultrafiltration is summarized by Kozinski and Lightfoot.[1]

> In reverse osmosis, the boundary layer is treated as an ideal dilute solution for which the pressure gradient will be zero. … In mechanical filtration, the solute is deposited … at the boundary. … The coefficient of the pressure gradient is now the hydrodynamic resistance of this sludge layer and can be obtained from conventional expressions for flow through porous media. … In ultrafiltration, both effects can be important … in concentrated solutions the pressure gradient cannot be neglected … .

Kozinski and Lightfoot indicated that pressure gradients due to transmitted elastic stress in ultrafiltration boundary layers must be accounted for in order to describe relative motion, and proposed a modified version of Darcy's law. However, Wales[2] later suggested that the pressure is constant in such layers and that Fick's law can be used. Two subsequent papers claimed to have proved the same result.[3,4] Two different groups have attempted to measure the pressure in ultrafiltration boundary layers. Kim *et al.*[5] measured the pressure drop across a layer containing the protein bovine serum albumin (BSA), and concluded that the pressure was constant. Zhang and Ethier[6] studied a layer containing the biopolymer hyaluronate (HA) and found a significant drop in pressure.

In the following sections we show that the above disagreement can be resolved by defining carefully, in terms of experimental measurements, what was meant by the word "pressure" in each case. In fact, several different meanings of the word are in use in the above works. By clearly defining these quantities, we are able to reconcile the theoretical disagreements, and obtain the remarkable result that Fick's and Darcy's laws are equivalent.

IV. PERVADIC PRESSURE

In this section we define the thermodynamic pressure P, the *pervadic* pressure p, and the generalized osmotic pressure Π. Consider a two-component mixture held within a rigid container (Fig. 3). The thermodynamic pressure P of the mixture is defined by the relation[15]

$$P \equiv -\left(\frac{\partial U}{\partial V}\right)_{S,M_k} \quad (k=1,2), \tag{4}$$

where U, V, S, and M_k are the internal energy, volume, entropy, and mass (of component k), respectively, of the mixture in Fig. 3. Thus, P is a measure of the change in internal energy associated with a change in volume. Experimentally,

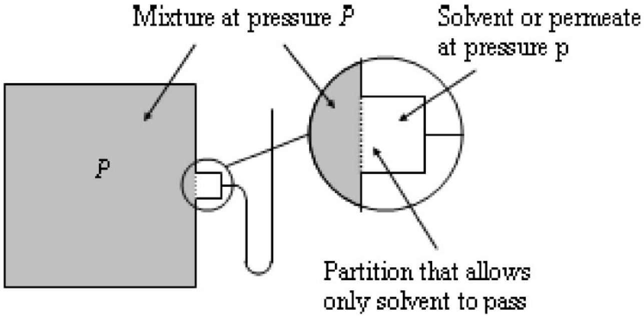

FIG. 3. Device used to measure the generalized osmotic pressure Π of a binary mixture at pressure P. The mixture (which can be a fluid solution, a gel, a porous medium, or a particulate suspension) is held within a rigid container at pressure P. Connected to the container by a partition is a manometer containing pure solvent or permeate at pressure p. The partition is held rigidly in place and is permeable only to the solvent. The osmotic pressure is defined as the difference between the pressure of the mixture P and the pervadic pressure p measured by the manometer.

P can be obtained by measuring the force per unit area exerted on the mixture in Fig. 3. As noted by Gibbs,[15] Eq. (4) applies to all mixtures at equilibrium, including fluids, solids, and solids which absorb fluids, as long as the mixture is under isotropic stress.

Connected to the system is a manometer. Only component 1 is able to pass into the manometer due to a rigid, semipermeable partition or sieve separating the manometer from the system. The pressure measured by the manometer is defined as the pervadic pressure p. The difference between the pressure P of the mixture and the pervadic pressure p is the generalized osmotic pressure of the mixture:

$$\Pi \equiv P - p. \tag{5}$$

Figure 4 shows how the pervadic pressure p can be measured in systems undergoing relative motion. (We assume the system in Fig. 4 is composed of mass elements that are homogeneous and, on the length and time scales of the measurement, in equilibrium with the measuring device. That is, we make the local equilibrium assumption.) In the case of porous media, p is identical to the pressure measured by Darcy.[10,11] However, component 2 need not be silica particles used by Darcy; it could also be a solution of salt ions or suspension of macromolecules; p is measured the same way in each case. (Note that in theories of porous media,[16] $P=-\sigma$, where σ is the isotropic portion of the total stress on the system, and $\Pi=-\sigma'$, where σ' is the isotropic stress on the porous matrix. The physical origin of these quantities is different in dilute solutions and porous media; however, the experimental definition, and hence the macroscopic nature of these quantities, is the same.)

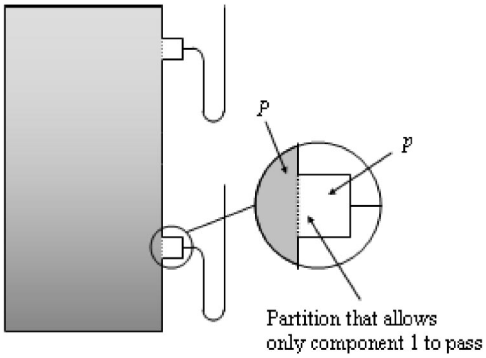

FIG. 4. Schematic showing measurements of the pervadic pressure p in a binary system experiencing relative motion. The measurement is meaningful if the region in front of the partition is homogeneous and in equilibrium with the measuring device. That is, the region is uniform and unchanging on the time and length scales of the measurement.

We have now defined the pressure of the mixture P, the pervadic pressure p, and the generalized osmotic pressure Π in terms of experimental measurements. Before introducing the sedimentation-diffusion equation, we consider briefly the effect of gravity on the system in Fig. 4. The condition for mechanical equilibrium in the presence of slow relative motion is (Sec. VI)

$$\nabla P = \rho \mathbf{g}, \tag{6}$$

where $\rho=\rho_1+\rho_2$ is the density (mass per unit volume) of the mixture. Equation (6) is assumed to apply also in theories of flow through elastic porous media,[16] where it is written, in the case of isotropic stress considered here, $\nabla\sigma+\rho\mathbf{g}=0$.

V. EQUIVALENCE OF FICK'S AND DARCY'S LAWS

Consider a suspension of spheres of constant radius R and density ρ_p. The dimensions of the particles are much larger than those of the intervening fluid molecules. The sedimentation-diffusion equation is a generalization of an equation used by Einstein to describe the motion of the spheres relative to the fluid:[17,18]

$$\frac{6\pi R\eta}{f}(\mathbf{v_2}-\mathbf{v^0}) = -\frac{1}{n}\nabla\Pi + \mathbf{K}. \tag{7}$$

Here $6\pi R\eta$ is the viscous resistance of a single sphere moving through the fluid, $f(n)$ is a friction factor accounting for the effect of particle-particle interactions on the viscous resistance, and n is the number of particles per unit volume; i.e.,

$$n = \frac{\phi}{v_p} = \frac{\rho_2}{m_p}, \tag{8}$$

where $v_p=\frac{4}{3}\pi R^3$ and $m_p=v_p\rho_p$ are the volume and mass, respectively, of a particle. The force $\mathbf{K}=v_p(\rho_p-\rho_f)\mathbf{g}$ is the net gravitational force acting on the particles. Equation (7) can be written as, with (8) and neglecting the effect of gravity,

$$\rho_2(\mathbf{v_2}-\mathbf{v^0}) = -\frac{f}{6\pi R\eta}\left(\frac{\partial\Pi}{\partial n}\right)\nabla\rho_2. \tag{9}$$

Equation (9) states that the mass flux of component 2 relative to the volume average velocity is a linear function of the concentration gradient, and is therefore equivalent to Fick's empirical law (1). Comparing these equations yields

$$D = \frac{f}{6\pi R\eta}\frac{\partial\Pi}{\partial n}. \tag{10}$$

Equation (10) is usually referred to as the generalized Stokes–Einstein relation, and was obtained by Onsager and

Fuoss.[19] In a dilute suspension particle-particle interactions can be neglected and the friction factor is equal to 1. The osmotic pressure of a dilute suspension is nk_BT, where k_B is Boltzmann constant and T is the absolute temperature. Equation (10) reduces, in this case, to the Stokes–Einstein relation of a dilute suspension,

$$D = \frac{k_BT}{6\pi R\eta}. \tag{11}$$

Equation (7) has found use in the study of the sedimentation and diffusion of suspended particles. For example, Davis and Russel[18] used this equation to study a suspension of silica particles. They first combined the sedimentation-diffusion equation with conservation of mass to model the volume fraction profile as silica spheres sedimented to the bottom of a closed container. Then they allowed fluid to permeate through the sedimented layer. As the particle radius R increased, the effect of Brownian diffusion became negligible, and the sedimentation and filtration process formed a close-packed layer of uniform concentration. The system studied by Davis and Russel, in the limit of large particles experiencing negligible Brownian diffusion, is identical to the system studied by Darcy. (Recall that Darcy first allowed a suspension of silica particles to sediment to the bottom of his container and then he allowed water to permeate through the system.) If Darcy's experimental system is a limiting case of the system studied by Davis and Russel, though, there must be a relation between Darcy's law and the sedimentation-diffusion equation.

In order to show that the two equations are equivalent we use the experimental definition of osmotic pressure $\Pi = P - p$ and the condition for mechanical equilibrium (6). Combining these two equations with (7) and (2) yields

$$\mathbf{q} = -\frac{1}{n}\frac{f}{6\pi R\eta}(\nabla p - \rho_f \mathbf{g}). \tag{12}$$

In obtaining (12) we also used the relation $\rho = (1-\phi)\rho_f + \phi\rho_p$, which is valid in the present case (constant ρ_p and ρ_f). Equation (12) states that the volume flux of component 1 relative to component 2 is a linear function of the quantity $\nabla p - \rho_f \mathbf{g}$, and is therefore equivalent to Darcy's empirical law (3). Since (12) is also equivalent to (7), it follows that in the absence of gravity Fick's and Darcy's laws are equivalent. Comparing (12) with (3) yields a relation between the permeability and the friction coefficient

$$\frac{k}{\eta} = \frac{1}{n}\frac{f}{6\pi R\mu}. \tag{13}$$

Combining (13) and (10) yields an alternative version of the Stokes–Einstein relation

$$D = n\frac{k}{\eta}\frac{\partial \Pi}{\partial n}. \tag{14}$$

Therefore, the transport coefficients D and k are not independent but are related via Eq. (14) to the same underlying physical variables. Whether one chooses to speak in terms of a diffusion coefficient or a permeability depends partly on convention and partly, for convenience perhaps, on the closeness of the particular system under consideration to a solution or a porous medium, respectively.

Before concluding this section we note that Hubbert published the first generally accepted derivation of Darcy's law in 1956.[11,20] Hubbert derived Darcy's law by averaging the Navier–Stokes equations over a network of interconnecting pores. The success of Hubbert's theory of flow through porous media (and later theories based upon his method[21,22]) has led to the view that Darcy's law should only be applied to systems experiencing slow viscous flow through a network of pores. Recently, however, Darcy's law has been applied to systems involving diffusion in colloidal and macromolecular solutions.[23–25] Our result lends theoretical support to such studies.

VI. IRREVERSIBLE THERMODYNAMICS

In this section we place the previous results within the basic framework of irreversible thermodynamics.[9,26,27] We consider a two-component mixture under isotropic stress, experiencing the irreversible processes of heat flow and slow relative motion of the components. Conservation of mass, momentum, and energy is expressed by the equations[9]

$$\rho\frac{dc_2}{dt} = -\nabla\cdot\mathbf{J_2}, \quad \frac{d\rho}{dt} = -\rho\nabla\cdot\mathbf{v}, \tag{15}$$

$$\rho\frac{d\mathbf{v}}{dt} = \nabla\cdot\mathbf{T} + \rho\mathbf{g}, \tag{16}$$

$$\rho\frac{du}{dt} = \mathbf{T}:\nabla\mathbf{v} - \nabla\cdot\mathbf{J_q}. \tag{17}$$

In Eqs. (15)–(17) $c_2 = \rho_2/\rho$ is the mass fraction of component 2, $d/dt = \partial/\partial t + \mathbf{v}\cdot\nabla$ is the material derivative, $\mathbf{J_2} = \rho_2(\mathbf{v_2} - \mathbf{v})$ is the mass flux of component 2 relative to the barycentric (mass-average) velocity $\mathbf{v} = c_1\mathbf{v_1} + c_2\mathbf{v_2}$, $\rho = \rho_1 + \rho_2$ is the density of the mixture, $\mathbf{T}$ is the stress tensor, $\mathbf{g}$ is the acceleration due to gravity, u is the internal energy per unit mass, and $\mathbf{J_q}$ is a flux of heat defined by Eq. (17).

For a mixture under isotropic stress $(\mathbf{T} = -P\mathbf{I})$ with slow relative motion of the components $(d\mathbf{v}/dt = 0)$ conservation of momentum and energy can be written as

$$\nabla P = \rho\mathbf{g}, \tag{18}$$

$$\rho\frac{du}{dt} = -P\nabla\cdot\mathbf{v} - \nabla\cdot\mathbf{J_q}, \tag{19}$$

where P is the thermodynamic pressure and $\mathbf{I}$ is the unit tensor.

As noted by Lhuillier,[27] a suspension of particles is different from a solution in that, one can often define and measure the volume and true density of an individual suspended particle (whereas the volume of a particle in a solution is not well defined). The partial mass densities of the suspension can then be written as $\rho_1 = \rho_f(1-\phi)$ and $\rho_2 = \rho_p\phi$, where ρ_f and ρ_p are the true densities of the fluid and particles, respectively, and ϕ is the local volume fraction of particles. In some suspensions, however, the true densities will not remain constant, but will be functions of temperature, pressure, and concentration (clay colloids, for example). In this case it is advisable to use the more general relations[28] $\rho_1\nu_1 = 1-\phi$ and $\rho_2\nu_2=\phi$, where ν_k is the partial specific volume of component k.[29]

According to the local equilibrium assumption,[9,26] a mass element of the mixture moving at the barycentric velocity is in equilibrium on the time scale dt, so that the Gibbs relation can be applied to the element followed along its center of mass motion:

$$T\frac{ds}{dt} = \frac{du}{dt} + P\frac{d\nu}{dt} - \mu_1\frac{dc_1}{dt} - \mu_2\frac{dc_2}{dt}. \tag{20}$$

In Eq. (20) T is the temperature, s is the entropy per unit mass, $\nu=1/\rho$ is the specific volume, and μ_k is the chemical potential per unit mass of component k. With the relation $c_1+c_2=1$, Eq. (20) can be written in the form

$$\rho\frac{ds}{dt} = \frac{\rho}{T}\frac{du}{dt} - \frac{P}{\rho T}\frac{d\rho}{dt} - \frac{(\mu_2-\mu_1)}{T}\rho\frac{dc_2}{dt}. \tag{21}$$

Inserting (15) and (19) into (21) yields a balance equation for the entropy[9]

$$\rho\frac{ds}{dt} = -\nabla\cdot\boldsymbol{J}_{\boldsymbol{s}} + \sigma, \tag{22}$$

where $\boldsymbol{J}_{\boldsymbol{s}}$ is the flux of entropy,

$$\mathbf{J_s} = \frac{1}{T}[\mathbf{J_q} - (\mu_2-\mu_1)\mathbf{J_2}], \tag{23}$$

and σ is the rate of production of entropy per unit volume,

$$T\sigma = -\mathbf{J_s}\cdot\nabla T - \mathbf{J_2}\cdot\nabla(\mu_2-\mu_1). \tag{24}$$

In an isothermal system Eq. (24) reduces to

$$T\sigma = -\mathbf{J_2}\cdot[\nabla(\mu_2-\mu_1)]_T, \tag{25}$$

where the subscript T indicates that the temperature is uniform. Near equilibrium, the flux $\mathbf{J_2}$ appearing in the expression (25) for production of entropy is assumed to be a linear function of the driving force $[\nabla(\mu_2-\mu_1)]_T$ yielding the equation[9]

$$\mathbf{J_2} = -L[\nabla(\mu_2-\mu_1)]_T \tag{26}$$

where $L=L(T,P,c_2)$ is a phenomenological coefficient.

Equation (26) is a purely thermodynamic relation expressing that a gradient in chemical potential will drive a flux of mass. It can be made more practical by writing it in terms of quantities that are actually measured. For example, using the Gibbs–Duhem equation

$$\rho_1(\nabla\mu_1)_T + \rho_2(\nabla\mu_2)_T = \nabla P \tag{27}$$

and the relation $(\nabla\mu_2)_T = \nu_2\nabla P + (\partial\mu_2/\partial c_2)_{T,P}\nabla c_2$ yields

$$\mathbf{J_2} = -L\frac{\rho}{\rho_1}\left[\left(\frac{\partial\mu_2}{\partial c_2}\right)_{T,P}\nabla c_2 + \left(\nu_2 - \frac{1}{\rho}\right)\nabla P\right]. \tag{28}$$

Equation (28) is an improvement on (26) as c_2 and P can usually be measured. Equation (28) suggests the definition of a diffusion coefficient[9]

$$D = \frac{L}{\rho_1}\left(\frac{\partial\mu_2}{\partial c_2}\right)_{T,P}, \tag{29}$$

which yields, with (18) and the relation $\rho_1\nu_1+\rho_2\nu_2=1$,

$$\mathbf{J_2} = -\rho D\nabla c_2 + \rho L(\nu_1-\nu_2)\mathbf{g}. \tag{30}$$

The flux in (30) includes two terms involving ∇c_2 (concentration diffusion) and $\mathbf{g}$ (sedimentation). In the absence of gravitational effects Eq. (30) reduces to Fick's law of diffusion:[9]

$$\mathbf{J_2} = -\rho D\nabla c_2. \tag{31}$$

In experiments in closed containers it can be more convenient to write the fluxes in terms of the volume average velocity $\mathbf{v^0} = \rho_1\nu_1\mathbf{v_1} + \rho_2\nu_2\mathbf{v_2}$ instead of the mass average velocity $\mathbf{v}$. Using the relations $\mathbf{J_2^0} = \rho_2(\mathbf{v_2}-\mathbf{v^0}) = \rho\nu_1\mathbf{J_2}$ and $(\partial\rho_2/\partial c_2)_{T,P} = \rho^2\nu_1$, Eq. (30) can be written in terms of the volume average velocity to yield

$$\mathbf{J_2^0} = -D\nabla\rho_2 + \rho_2 s_d\mathbf{g}, \tag{32}$$

where $s_d = L\rho^2\nu_1(\nu_1-\nu_2)/\rho_2$ is the sedimentation coefficient.[9,30]

In some experiments, particularly those involving filtration, it is more convenient to measure the pervadic pressure p (Fig. 4) than the concentration. The pervadic pressure can be related to the chemical potential of component 1 by considering an experiment at constant temperature in which the thermodynamic pressure P and concentration c_2 of the mixture in Fig. 3 are varied. If P, c_2, and the pressure p of the pure fluid in the manometer are changed in such a manner that equilibrium between the mixture and the manometer is maintained we must have, throughout the process,

$$(d\mu_1)_T = (d\mu_1^0)_T, \tag{33}$$

where μ_1^0 is the chemical potential of pure component 1 in the measuring device. For an isothermal process,

$$(d\mu_1^0)_T = \nu_1^0 dp, \tag{34}$$

where $\nu_1^0 = 1/\rho_f$ is the specific volume of pure component 1. With the local equilibrium assumption Eqs. (33) and (34) can be combined to yield

$$(\nabla\mu_1)_T = \frac{1}{\rho_f}\nabla p. \tag{35}$$

Combining (35), (27), and (18), and the relation $\mathbf{q} = \rho_1\nu_1(\mathbf{v_1}-\mathbf{v_2}) = -\rho\nu_1\mathbf{J_2}/\rho_2$ with (26) yields Darcy's law,

$$\mathbf{q} = -\frac{k}{\eta}(\nabla p - \rho_f\mathbf{g}), \tag{36}$$

where η is the viscosity of pure component 1 and k is the permeability,

$$\frac{k}{\eta} = L\left(\frac{\rho}{\rho_2}\right)^2\left(\frac{\nu_1}{\rho_f}\right). \tag{37}$$

Equations (36) and (32) are each equivalent to (26), but are more practical in that they are written in terms of measurable quantities. Which equation is used in a particular situation depends upon the particular experimental setup and upon whether it is found more convenient to measure changes in concentration or changes in pervadic pressure.

Combining (37) and (29) yields a relation between the diffusion coefficient and the permeability,

$$D = \frac{k}{\eta}\frac{\rho_2^2\rho_f}{\rho_1}\left(\frac{\partial\mu_2}{\partial\rho_2}\right)_{T,P}, \tag{38}$$

where the relation $(\partial\rho_2/\partial c_2)_{T,P}=\rho^2\nu_1$ has been used. The chemical potential is related to the osmotic pressure via equation[28] $(\partial\mu_2/\partial\rho_2)_{T,P}=(\rho_1\nu_1/\rho_2)(\partial\Pi/\partial\rho_2)_{T,\mu_1}$, so that (38) can be written as

$$D = \rho_2\frac{k}{\eta}(\rho_f\nu_1)\left(\frac{\partial\Pi}{\partial\rho_2}\right)_{T,\mu_1}. \tag{39}$$

In a suspension of hard-sphere particles $\nu_1=1/\rho_f$ and $\rho_2=nm_p$, where m_p is the constant mass of a particle, in which case Eq. (39) reduces to (14). This provides a connection between the thermodynamic theory developed here and the hard-sphere theory presented in Sec. V.

VII. "MODIFIED" DARCY'S LAW

It is a common objective in the study of macromolecular solutions and gels to separate the effects of elastic stress (due to the forces the macromolecules exert on each other) from the effects of the particles' random, or Brownian, motion.[31–35] One way to obtain such a separation is to assume that the generalized osmotic pressure Π can be decomposed into an elastic contribution $-\sigma'$ and a mixing contribution π:[36–39]

$$\Pi = \pi + (-\sigma'). \tag{40}$$

Much work in polymer physics is directed toward obtaining theories and measurements of σ' and π.[31,40,41]

Combining (40) with (39) yields $D=D^m+D^{\mathrm{el}}$, where $D^m=\rho_2(k/\eta)(\partial\pi/\partial\rho_2)$ is the Brownian portion of the diffusion coefficient and $D^{\mathrm{el}}=\rho_2(k/\eta)[\partial(-\sigma')/\partial\rho_2]$ is the elastic portion (the approximation $\nu_1\approx 1/\rho_f$ is a good one in many systems). A dimensionless number $N=D^{\mathrm{el}}/D^m$ governs the relative magnitude of the two effects. For dilute suspensions and solutions, $N=0$, and relative motion (in the absence of gravity) is driven solely by Brownian diffusion. For a close-packed matrix of hard spheres (a porous medium) $1/N=0$ and relative motion is driven by the presence of a gradient in elastic stress. For concentrated suspensions and gels N will take on some finite value. The magnitude of N could be used to indicate whether it will be more convenient to use Fick's law ($N\ll 1$) or Darcy's law ($N\gg 1$) in a particular system. In Sec. VIII we approximate D^{el}, D^m, and N within a macromolecular solution.

Given the above separation of elastic and Brownian effects, one can define

$$p^m \equiv P - p^{\mathrm{el}}, \tag{41}$$

where $p^{\mathrm{el}}\equiv-\sigma'$. Thus, p^m is equal to the pressure of the mixture as a whole less the pressure due to the isotropic elastic stress supported by component 2. Let us discuss the nature of this quantity, p^m. In the limit of a saturated close-packed matrix of hard spheres, i.e., a porous medium, Brownian diffusion is absent and $\pi=0$. In this case Eqs. (41), (5), and (40) can be combined to yield

$$p^m = p. \tag{42}$$

Thus, for porous media, p^m is equal to the pervadic pressure measured by Darcy. In a dilute suspension, however, the particles exert no forces on each other and $\sigma'=0$. Equation (41) yields

$$p^m = P. \tag{43}$$

Therefore, during Brownian diffusion in dilute suspensions p^m is equal to the pressure of the mixture as a whole and is therefore constant (neglecting the effects of gravity). During relative motion in concentrated solutions and suspensions, p^m will not remain constant, as was pointed out by Kozinski and Lightfoot[1] (Sec. III).

Combining (41), (5), and (40) with (36) yields

$$(1-\phi)(\mathbf{v_1}-\mathbf{v_2}) = -\frac{k}{\eta}(\nabla p^m - \nabla\pi - \rho_f\mathbf{g}). \tag{44}$$

Or, if $\mathbf{v_2}=0$ and gravity is neglected,

$$(1-\phi)\mathbf{v_1} = -\frac{k}{\eta}(\nabla p^m - \nabla\pi). \tag{45}$$

Equation (45) has been referred to as the "modified" Darcy's law,[4,42,43] although, as we have shown, it is in fact equivalent to Darcy's law. Combining (44) with (13) and the Stokes–Einstein relation for D^m yields

$$\mathbf{J_2^0} = -D^m\nabla\rho_2 + \rho_2\frac{k}{\eta}(\nabla p^m - \rho_f\mathbf{g}). \tag{46}$$

The first term on the right-hand side of (46) describes the mass flux due to Brownian motion of the particles and the second term describes the flux due to a gradient in elastic stress. This equation was used to obtain predictions of p^m in a system containing the biopolymer hyaluronate, which were consistent with the results of later experiments.[6]

VIII. IMPLICATIONS FOR ULTRAFILTRATION

The conceptual difficulty surrounding pressure in ultrafiltration processes can be resolved by distinguishing between the thermodynamic pressure P of the mixture and the pervadic pressure p that was measured by Darcy. The pervadic pressure will not remain constant during relative motion, even in ideal dilute solutions undergoing Brownian diffusion. (This can be tested by measuring the pervadic pressure during Brownian diffusion using the apparatus in Fig. 4.) The pressure P of the mixture as a whole, however, is determined by the condition for mechanical equilibrium (18) (assuming isotropic stress and slow relative motion). Neglecting the effects of gravity, P remains constant. The pressure p^m will remain constant in dilute solutions, but not in concentrated systems or porous media. If the mutual diffusion coefficient D is known and gravity is absent, it is not necessary to calculate or measure any of the above pressures. However, it may be more convenient in some systems to use Darcy's law (or a version of the "modified" Darcy's law), and hence predict the pressure profile. (The dimensionless

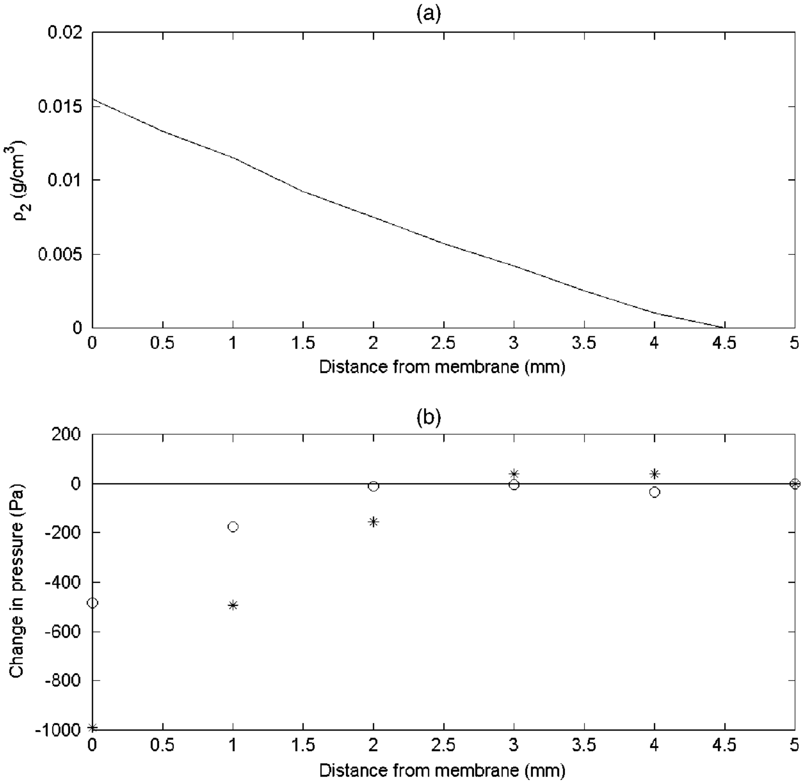

FIG. 5. Steady state (a) concentration and (b) pressure measurements of Ethier *et al.* (Refs. 6 and 42) in a filtration boundary layer containing the biopolymer hyaluronate. [The concentration measurements of Zhang and Ethier (Ref. 6) were actually of c_2, the mass fraction of hyaluronate. They did not measure ρ_2. However, as noted by Gowman and Ethier (Ref. 42), the density ρ of the mixture remained very near 1 g/cm^3 during the experiment, so that ρ_2 can be used in place of c_2.] The two sets of symbols in (b) represent two separate traverses of the layer with a pressure transducer. The diamonds and squares represent an average of the data taken during the first and second traverses, respectively.

number N introduced in Sec. VII can be used to indicate which of Fick's and Darcy's laws will be more convenient in a particular system.) Also, measuring or calculating p (and/or p^m) can yield useful information about the system, as we show below.

We consider the implications of the above results for the pressure measurements of Kim *et al.*[5] and Zhang and Ethier[6] mentioned in Sec. III. Both of these groups were attempting to measure the pressure p^m, and thereby determine if any elastic stress was present in their system. However, there is at present no unambiguous method for the measurement of p^m. In both of the experiments, the measurements were performed by inserting a pressure transducer into the layer and taking readings at different positions. The pressure transducer used in the experiments consisted of a tip connected to a base held at a constant reference pressure. As the pressure in the mixture changes, the position of the tip changes relative to the base, allowing measurements to be made. The radius of the tip was ≈1 mm, whereas the size of the macromolecules was on the order of 0.1 μm.[4] Since the size of the sensing tip was much larger than the size of the particles, it would seem both Kim *et al.* and Zhang and Ethier actually measured the pressure of the mixture P. If they did indeed measure P, the pressure should have remained constant, or perhaps increased slightly due to the effects of gravity. Kim *et al.*[5] took measurements within a layer containing the protein bovine serum albumin (BSA; molecular weight 65 000 Da) and found that the pressure remained constant (to within experimental error).

However, this explanation does not account for the experiment of Zhang and Ethier,[6] who measured a *drop* in pressure across a layer containing the biopolymer hyaluronate (HA, molecular weight 10^6 Da). Figure 2 represents the system studied by Zhang and Ethier. Above the partition (a polycarbonate membrane) was placed a small amount of hyaluronate solution, above which was placed pure solvent (0.01M NaCl). At $t=0$ a pressure P was applied to the system above the membrane, generating a flux of mass. Eventually a steady state was reached. Two experiments were then performed on the system. In the first, the concentration of hyaluronate at different points within the steady state layer was measured using a light refraction technique [Fig. 5(a)]. In the second, the steady state pressure profile was measured [Fig. 5(b)].

At steady state, the velocity v_2 of the hyaluronate is zero everywhere and Fick's law (1) can be written as

$$D = \rho_2 v^0 \bigg/ \frac{d\rho_2}{dx}. \tag{47}$$

All of the quantities on the right-hand side of (47) were measured by Ethier *et al.* Therefore, they were able to predict the diffusion coefficient as a function of ρ_2. The results are plotted in Fig. 6(a).

It was suggested that the nonlinearities in Fig. 6(a) may have been due to a transition from a relatively dilute concentration regime to a regime in which the hyaluronate particles begin to entangle.[44] This transition is known to occur somewhere in the range $0.004 \leq \rho_2 \leq 0.01$ g/cm^3.[44,45] Thus, there is the possibility that the entangled HA molecules were prohibited from contributing to Zhang and Ethier's pressure measurement. (BSA is a compact globular protein and is much less prone to entanglement.) One may now reasonably ask if Zhang and Ethier measured the pressure p^m. We cannot

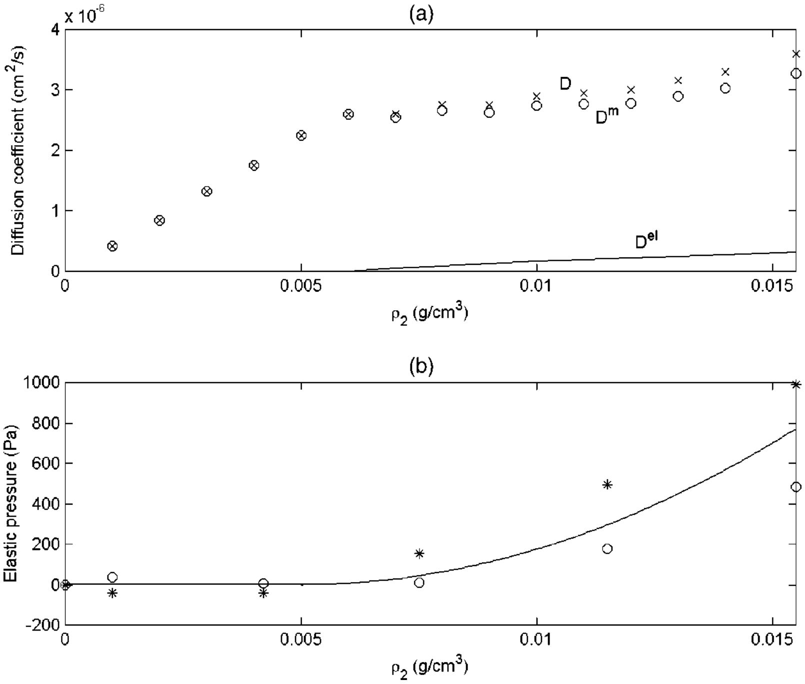

FIG. 6. (a) Measurements of the diffusion coefficient D of the biopolymer hyaluronate obtained by Ethier *et al.* (Refs. 42 and 44). (b) Prediction of the elastic pressure $p^{\mathrm{el}}=-\sigma'$ obtained using Eq. (41) and Zhang and Ethier's (Ref. 6) measurements of p^m. The solid line is a polynomial fit. Also shown in (a) are the mixing and elastic portions of the diffusion coefficient predicted using the Stokes–Einstein relation and the data for D and p^{el}.

be certain that they measured this pressure. In all likelihood they measured some combination of p^m and P. However, given that such a measurement was their intention, and given the potential of such measurements to distinguish between the effects of Brownian motion and elastic stress, we feel it is worthwhile exploring the consequences of assuming they did indeed measure p^m.

Neglecting the effects of gravity within the layer, the equation $p^{\mathrm{el}}=P-p^m$ can be used to obtain a prediction of the elastic pressure $p^{\mathrm{el}}=-\sigma'$ due to the stress (assumed isotropic) supported by the entangled HA molecules [Fig. 6(b)]. At low concentration, there is no elastic stress; hyaluronate diffuses like a dilute suspension and p^{el} is zero. However, at a concentration corresponding to entanglement ($\sim 0.006\ \mathrm{g/cm^3}$), the elastic pressure starts to increase from zero and continues to increase with increasing concentration. These predictions could in future be tested by measuring the elastic stress σ' directly (for example, via quasielastic light scattering[40,41]).

A fit of $p^{\mathrm{el}}(\rho_2)$, along with Ethier's[46] estimate (from sedimentation studies) of the permeability, $k=2.92\times 10^{-16}\rho_2^{-1.47}(\mathrm{cm}^2)$, yields the elastic portion of the diffusivity $D^{\mathrm{el}}=\rho_2(k/\eta)(\partial p^{\mathrm{el}}/\partial \rho_2)$ and hence the mixing portion $D^m=D-D^{\mathrm{el}}$. These quantities are plotted on Fig. 6(a) along with measurements of D by Ethier *et al.* Apparently entanglement significantly hinders the effect of Brownian diffusion on relative motion, with only moderate compensation from elastic stress. These predictions could also be tested using quasielastic light scattering measurements of D^m.

We can now approximate the dimensionless number $N=D^{\mathrm{el}}/D^m$ introduced in Sec. VII. From Fig. 6(a) it is evident that $N<0.1$ over the entire concentration range used in the experiment of Ethier *et al.* As this value is less than 1, we anticipate that it will be more convenient to use Fick's law as the constitutive relation. This does not, however, rule out the use of Darcy's law. There may be other reasons to characterize the system using Darcy's law.

It would, first of all, be interesting to measure p using an apparatus like that in Fig. 4. Such measurements could be used experimentally to determine permeability (as well as to provide an experimental test of the equivalence of Fick's and Darcy's laws). Alternatively, predicting p (given an independent determination of the permeability) can yield an estimate of the amount of fouling. That is, in the experiments of Ethier *et al.*, it was suspected that the hyaluronate tended to become adsorbed or lodged within the pores of the membrane. Following Gowman and Ethier,[42] we can gain an estimate of the effect of the fouling on the pressure required to pass solvent through the system by predicting the drop in pervadic pressure across the layer, and comparing this value with the measured drop in pressure of the pure solvent across the entire system. Using Gowman and Ethier's measurement of the concentration profile and the volume flux at steady state, along with Ethier's[46] estimate of the permeability, Darcy's law can be integrated across the layer to yield $\Delta p_{\mathrm{layer}}=17\ \mathrm{kPa}$. (This prediction could be tested by measuring $\Delta p_{\mathrm{layer}}$ using an apparatus like that in Fig. 4.) The total pressure drop experienced by the solvent across the entire system was measured as $\Delta p_{\mathrm{tot}}=56\ \mathrm{kPa}$.[42] And the drop in pressure required to pass pure solvent across the membrane (with no HA present) was measured as $\Delta p_{\mathrm{mem}}=6\ \mathrm{kPa}$. Therefore, the drop in pervadic pressure attributable to fouling of the membrane was

$$\Delta p_{\mathrm{foul}}=\Delta p_{\mathrm{tot}}-\Delta p_{\mathrm{layer}}-\Delta p_{\mathrm{mem}}=33\ \mathrm{kPa}. \tag{48}$$

This estimation, more than half of the total pressure drop, is consistent with Gowman and Ethier's expectation of significant blockage of the membrane pores in their system.

IX. CONCLUSION

In summary, the thermodynamic pressure P of the mixture remains constant during relative motion, as long as the effects of gravity are negligible and the condition for mechanical equilibrium (18) is satisfied. The pressure p^m introduced by Kozinski and Lightfoot[1] is constant in dilute systems, but varies if elastic stress is present. Kim *et al.*[5] and Zhang and Ethier[6] attempted to measure p^m. Kim *et al.* actually measured P and found that it was constant. Zhang and Ethier may have measured p^m. Neither group attempted to determine the pervadic pressure p which was measured originally by Darcy.[10] If a group were to measure the concentration and pervadic pressure simultaneously, it would provide a direct experimental test of the equivalence of Fick's and Darcy's laws.

In this paper we have defined the pressure measured by Darcy on a thermodynamic and experimental basis. As a consequence, we have shown that Fick's and Darcy's laws are equivalent. The range of applicability of both equations is therefore increased. We used this result to reconcile apparent contradictions in theoretical claims and to provide a new interpretation of experiments in ultrafiltration.

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[29] The partial specific volume of component 2 is defined by the equation $\nu_2=(\partial V/\partial M_2)_{T,P,M_1}$, where V is the volume of a system at equilibrium (or a volume element in local equilibrium) and M_2 is the mass of component 2. (The partial specific volume of component 1 is defined analogously.) Thus, ν_2 is a measure of the change in volume of the mixture due to a small increase in mass of component 2, with the temperature, pressure, and mass of component 1 held constant. In general, the partial specific volumes are not constant; i.e., $\nu_k=\nu_k(T,P,c_2)$. However, for a suspension of particles having constant true densities, $\nu_2=\nu_2^0=1/\rho_p$ and $\nu_1=\nu_1^0=1/\rho_f$, where ν_k^0 is the specific volume of pure component k.

[30] The sedimentation coefficient is defined as the ratio of the sedimentation velocity to the acceleration due to gravity during sedimentation of a uniform suspension ($\nabla\rho_2=0$) in a closed container ($\mathbf{v}^{\mathbf{0}}=0$); that is, $s_d=\mathbf{v}_2/\mathbf{g}$.

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