

COMMENTS ON THE DEBIJE-BRINKMAN EQUATION

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We present a macroscopic derivation of the Debye-Brinkman equation for the flow of a fluid through a polymer coil. By using an exact relation between the sedimentation coefficient and the permeability it is found that the permeability of the coil is strongly dependent on the nature of the fluid, due to local clustering of the polymer segments.

The hydrodynamics of a dilute polymer solution has been the subject of many investigations. These ultimately aim at expressing the transport coefficients of the solution in terms of the molecular weight and chemical composition of the polymer and the interaction between polymer and solvent. Debye¹⁾ and Brinkman²⁾ were the first to postulate that the flow of the solvent is determined in the stationary state by the equation

$$-\nabla P + \eta_0 \Delta V - (\eta_0/k)(V - U) = 0, \quad (1)$$

which we call the Debye-Brinkman equation, and by the relation

$$\operatorname{div} V = 0, \quad (2)$$

which expresses the incompressibility of the solvent. In these equations V , U and P denote the local velocity of solvent and solute and the local pressure. The viscosity of the pure solvent is denoted by η_0 , and the local permeability by k .

Operationally the permeability is defined by an experiment in which the solvent flows through a porous plug (a medium containing homogeneously distributed material in fixed positions) with a constant velocity V . The pressure gradient needed to accomplish this situation is given by Darcy's law

$$-\nabla P = (\eta_0/k) V \quad (3)$$

Recently Felderhof and Deutch³⁾ and Felderhof⁴⁾ presented a microscopic derivation of an equation very similar to eq (1), and calculated the most important transport coefficients. Their work may be considered as an extension of the microscopic treatment of Kirkwood and Riseman. Representing the polymer by a cloud of segments with number density $\varrho(t)$ and assuming a friction constant ζ per segment, Felderhof and Deutch derive an equation which is identical to the Debye-Brinkman equation provided the permeability is related to the segment density by

$$\eta_0 k = \zeta \varrho \quad (4)$$

However, this form of the Debye-Brinkman equation still contains the unknown microscopic quantity $\zeta \varrho$ and is, therefore, from a practical point of view, not yet an adequate starting point for the quantitative calculation of the transport coefficients. Actually, the a priori calculation of $\zeta \varrho$ from the molecular constitution of solute and solvent is a difficult and at present unsolved problem.

In this note we present a macroscopic derivation of the Debye-Brinkman equation (1) and we give an exact relation between the permeability and the sedimentation coefficient. In this way the equation is written in terms of the sedimentation coefficient, which can be measured accurately.

The system considered is a mixture of the solvent (mass density C_0) and solute (mass density C_1). These two local densities $C_0(\mathbf{r})$ and $C_1(\mathbf{r})$ are macroscopic densities, i.e. they are averages of the corresponding microscopic densities over

- 1) a spatial region the linear dimension of which (L) is large compared to the size of a repeating unit of a polymer, but small compared to the diameter of a polymer,
- 2) a time interval the length of which (T) is large compared to the relaxation time of part of the polymer chain enclosed in a volume L^3 , but small compared to a characteristic time of the imposed motion.

The microscopic velocity $\mathbf{v}(\mathbf{r})$ and pressure $p(\mathbf{r})$ of the fluid form that solution of the Navier-Stokes equation

$$-\nabla p + \eta_0 \Delta \mathbf{v} = 0 \quad (5)$$

which fulfills the many boundary conditions on the particles and the walls of the container (here we considered the stationary state and neglected the inertial term). The macroscopic velocity $\mathbf{V}(\mathbf{r})$ and pressure $P(\mathbf{r})$ can be obtained by averaging $\mathbf{v}(\mathbf{r})$ and $p(\mathbf{r})$ over the space-time domains $L^3 T$ discussed before. For these macroscopic fields the Navier-Stokes equation will hold in its usual form

$$-\nabla P + \eta_0 \nabla^2 \mathbf{V} + \mathbf{F} = 0, \quad (6)$$

where \mathbf{F} denotes the external force exerted on the solvent per unit volume.

In the case under consideration this force is only due to the solute *i.e.* F has to be identified with the total force which the solute exerts on the solvent per unit volume. Hence F could more appropriately be called a quasi external force. The concept of quasi external forces is not at all new. More than fifty years ago already these were introduced in the theory of colloidal electrolytes⁵⁾. The flow of liquid around a selected charged particle was described by means of eq. (6) with F replaced by σE the product of the charge density of the liquid and the electrostatic field strength.

The force F which the solute exerts on the solvent per unit volume can be calculated in the following way. Firstly, this force will depend only on the relative velocity ($V - U$) of the solvent with respect to the solute. Hence one can calculate F for a situation in which the solute is at rest and in which the solvent has a constant velocity $V - U$ everywhere. For such a situation (6) reduces to

$$-\nabla P_0 + F = 0 \quad (7)$$

But in this case Darcy's law eq. (3) gives

$$-\nabla P_0 = (\eta_0/k)(V - U) \quad (8)$$

Combination of the last two equations gives the expression

$$F = -(\eta_0/k)(V - U) \quad (9)$$

for the force exerted on the solvent per unit volume. When this result is substituted into (6) one finds the Debye-Brinkman equation (1).

Finally we would like to remark that the permeability can be expressed in terms of the sedimentation coefficient s by the relation

$$\frac{\eta_0}{k} = \frac{C_1}{s} \left(1 - \frac{v_1}{v_0} \right) C_0 v_0 \quad (10)$$

Here v_0 denotes the volume of a unit mass of the solvent and v_1 the volume of a unit mass of polymeric material. As $C_1 \ll 1$ the product $C_0 v_0$ is practically equal to unity and can be omitted. A derivation of (10) by using the formalism of irreversible thermodynamics can be found in a paper by Mijnlieff and Jaspers⁶⁾. This relation is very useful, because for the systems considered sedimentation coefficients can be determined much more easily and accurately than permeabilities. Using (10) the permeability of poly- α -methylstyrene in cyclohexane and toluene at various temperatures and concentrations was determined by Mijnlieff and Jaspers⁶⁾, some results are reproduced in table I. It is remarkable that the permeability of one and the same polymer is about three times higher in the 'poor' solvent cyclohexane than in the 'good' solvent toluene. This very specific solvent effect

might be ascribed to a local clustering of the repeating units of the polymer when in contact with a poor solvent. As a result the pores between these clusters, through which the solvent has to find its way, become wider, which leads to a steep increase in the permeability. This interpretation was supported⁶⁾ by the way in which the observed permeabilities appear to depend on the temperature.

TABLE I

Permeability of poly- <i>v</i> -methylstyrene at $C_1 = 1.64$ g/100 ml in cyclohexane and toluene at different temperatures. From Mijnlief and Jaspers ⁶⁾			
Temp (C)	$10^{12}k$ (cm ²)	Temp (C)	$10^{12}k$ (cm ²)
<i>In cyclohexane</i>		<i>In toluene</i>	
35	1.06	25	0.33
40	0.89	45	0.34
50	0.70	65	0.36
80	0.60	85	0.36
95	0.56	105	0.37
110	0.60	120	0.40
125	0.61		

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