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Abstract. — The diffusion mass flux in a mixture is usually written as the gradient of a chemical potential difference. When generalized to a solution of deformable polymers, this Fick’s law leads to difficulties and, on the basis of a kinetic theory approach, Sekhon, Armstrong and Jones recently suggested that that part of the mass flux which depends on the polymer deformation could be written as the divergence of a second-rank tensor. Our aim here is to consider a mixture of polymers and solvent with two different velocities, and with the help of macroscopic thermodynamics, to determine the assumptions leading to each of the two proposed expressions. We then show how the Soret effect and the deformation-induced diffusion are different for the two fluxes. Thus an experimental determination of the right proposal should, in principle, be easy to perform.

1. Introduction. — The anomalous retention of polymer molecules inside a porous medium [1-3] or the strange rheological effects observed in a capillary flow [4-6] led to the conclusion that a polymer solution is likely to exhibit spatial concentration gradients in a non-homogeneous flow. The origin of this migration has been long attributed to the deformation entropy of the molecules [7-8] which results in a force driving the polymers towards the regions of lowest stresses, i.e. the regions where the molecules are less deformed.

On the other hand, experiments on DNA molecules in a circular Couette flow [9] demonstrated a migration of these (rather rigid) molecules towards the rotating inner cylinder, the very place where the stress is highest. A second explanation was then proposed [10-11] which links migration to a purely viscous force, the so-called Faxen’ force which is a modified form of Stokes’ law in a non-homogeneous velocity field [12].

Among polymer physicists, the supporters of the viscous force and those of the entropic force form two orthogonal groups. As if this situation was not controversial enough, Sekhon, Armstrong and Jones [13] recently suggested that the hydrodynamic interactions inside the polymer molecules were responsible for a new force (hereafter called the SAJ force) leading to another possibility for polymer migration.

It is noteworthy that the SAJ and Faxen forces can be derived within the dumbbell model for polymers while the entropic force cannot. This is all the more surprising since the entropic force is nothing but a mere generalization of the famous Fick’s law to the case of a solution of deformable particles. This situation is rather puzzling and the purpose of this paper is to reconsider the mechanisms of polymer migration with the help of thermodynamics. We will not deal at length with the Faxen’s force since it is rather well known and exists even for a rigid particle. Here we focus upon the forces directly depending on the
polymer deformation and the results we arrive at with our thermodynamic approach are twofold.
- Firstly we determine the (mutually exclusive) hypotheses leading to the entropic force on the one hand, and to a SAJ-like force on the other hand.
- Secondly we find an explicit expression for these forces in terms of the polymer deformation. For the entropic force this is the expression already found by Tirrell and Malone [14]. For the SAJ force the result is new.

2. The free enthalpy of a dilute polymer solution. —

The free enthalpy per unit volume of a solution of polymer molecules embedded in a solvent can be written as

\[ G = \rho_p \mu_p + \rho_s \mu_s + \Delta G_m + \Delta G_d + \Delta G_k \]  

where \( \rho_p \) is the polymer mass per unit volume of the solution, \( \mu_p \) is the chemical potential per unit mass in a pure polymer phase while the index \( s \) characterizes the same quantities for the solvent.

\( \Delta G_m \) is the free enthalpy of mixing; we have a rather complete knowledge of it [15] but we only need its limiting form for dilute solutions (the case we consider henceforth)

\[ \Delta G_m = kT \frac{\rho_p}{m_p} \log \frac{\rho_p}{\rho_p^0} \]  

where \( m_p \) is the molecular mass of the polymer and \( \rho_p^0 \) the mass per unit volume of the pure polymer phase. Hence \( \rho_p/\rho_p^0 \) is the volume fraction of the polymers and \( \rho_p/m_p \) is the number of polymers per unit volume of the solution.

\( \Delta G_d \) is the free enthalpy of deformation. For a polymer in a « bad » solvent, \( \Delta G_d \) may be approximated as the deformation entropy of a Gaussian chain [16]. When the deformation is slight, as is the case in Poiseuille or Couette flow, Flory's complete expression merges into the simple result [17]

\[ \Delta G_d = \frac{1}{2} kT \frac{\rho_p}{m_p} (C_{ij} - \delta_{ij})^2 \]  

where

\[ C_{ij} = \frac{3 \langle r_i r_j \rangle}{r_0^2} \]

is the adimensional shape of the polymers and \( r_0 \) their equilibrium radius of gyration. For a polymer in a « good » solvent, the interactions between the monomers can be represented phenomenologically by considering \( r_0 \) as some function of the temperature and in this case \( \Delta G_d \) can no longer be thought of as a purely entropic contribution.

Lastly \( \Delta G_k \) is a kinematic contribution occurring when the velocities \( V_p \) and \( V_s \) are different from the centre of mass velocity \( V \) defined as

\[ \rho V = \rho_p V_p + \rho_s V_s \]  

with

\[ \rho = \rho_p + \rho_s \] .

If we neglect any « added mass » effect, i.e. the extra kinetic energy obtained by the solvent because of the polymer motion, we can simply write

\[ \Delta G_k = \frac{1}{2} \rho_p (V_p - V)^2 + \frac{1}{2} \rho_s (V_s - V)^2 \]

\[ = \frac{1}{2} \rho \frac{\rho_s}{\rho} (V_p - V_s)^2 \]  

The differential form of the free enthalpy is then

\[ dG = \mu_p \, d\rho_p + \mu_s \, d\rho_s - S \, dT + \alpha_{ij} \, dC_{ij} + P_i \, dw_i + dp \]  

where \( p \) is the pressure while for dilute solutions, we have

\[ \mu_p = \frac{\partial G}{\partial \rho_p} = \mu_p^0 + \frac{kT}{m_p} \left( \log \frac{\rho_p}{\rho_p^0} + \frac{1}{2} (C_{ij} - \delta_{ij})^2 \right) \]  

\[ + \frac{1}{2} (V_p - V)^2 \]  

\[ \mu_s = \frac{\partial G}{\partial \rho_s} = \mu_s^0 + \frac{1}{2} (V_s - V)^2 \]  

\[ S = \frac{1}{\rho} \frac{\partial G}{\partial \rho} = \rho_p s_0^p + \rho_s s_0^s - k \frac{\rho_p}{m_p} \left( \log \frac{\rho_p}{\rho_p^0} + \frac{1}{2} (C_{ij} - \delta_{ij})^2 \right) \]  

where \( s_0^s \) is the specific entropy of a pure phase,

\[ \alpha_{ij} = \frac{\partial G}{\partial C_{ij}} = kT m_p \rho_p (C_{ij} - \delta_{ij}) \]  

and

\[ P_i = \frac{\partial G}{\partial w_i} = \rho_p \rho_s \frac{w_i}{\rho} \approx \rho_p w_i \]

with

\[ w = V_p - V_s \] .

If we now consider the total energy

\[ U = G + TS - p + \frac{1}{2} \rho V^2 \]

we deduce from equation (6) the so-called Gibbs relation

\[ T \, dS = dU - \left( \mu_p - \frac{V_p^2}{2} \right) d\rho_p - \left( \mu_s - \frac{V_s^2}{2} \right) d\rho_s - \alpha_{ij} \, dC_{ij} - P_i \, dw_i - V_i \, d(\rho V_i) \]  

3. The entropy production (first stage). — To describe the evolution in time of the solution we must have an evolution equation for each of the thermo-
dynamic variables $\rho_p, \rho_s, \rho V_i, U, w_i$ and $C_{ij}$. Galilean invariance is satisfied with the following equations

$$\frac{\partial \rho_p}{\partial t} + V \cdot (\rho_p V + J) = 0$$

(14)

$$\frac{\partial \rho_s}{\partial t} + V \cdot (\rho_s V - J) = 0$$

(15)

$$\frac{\partial \rho V}{\partial t} + V \cdot (\rho V V + \overline{\pi}) = \rho g \quad (\pi_{ij} = \pi_{ij})$$

(16)

$$\frac{\partial U}{\partial t} + V \cdot (U V + V \cdot \overline{\pi} + Q) = \rho g \cdot V$$

(17)

$$\frac{\partial w}{\partial t} + (V \cdot V) w = F - \overline{\pi} \cdot T,$$

(18)

$$\frac{\partial C}{\partial t} + (V \cdot V) C = \overline{\pi}.$$

(19)

Combining these equations with the Gibbs relation (13) we can derive the balance equation for the entropy

$$\frac{\partial S}{\partial t} + V \cdot (SV + S) = -\frac{1}{T} [S V T + J \cdot V (\mu_p - \mu_s) + F \cdot P +$$

$$+ (\overline{\pi} - pT) : \overline{VV} + \overline{T} : \overline{VP} + \overline{R} : \overline{\alpha}]$$

(20)

where the entropy flux $S$ is defined as

$$TS = Q - (\mu_p - \mu_s) J - P \cdot \overline{T}.$$  

(21)

At this point, the usual procedure is to deduce from the entropy production (the right-hand side of eq. (20)) the expressions for the hitherto unknown fluxes $(S, J, F, \overline{\pi}, \overline{\pi}$ and $\overline{R})$ as functions of the thermodynamic forces $(V T, V (\mu_p - \mu_s), P, \overline{VV}, \overline{VP}$ and $\overline{\alpha})$. The resulting expressions are very complicated if one looks for completeness. Here we shall adopt a somewhat different approach by referring to the dumbbell model to get a sound expression for the flux $\overline{R}$, and by proposing plausible expressions for $J, S$ and $\overline{\pi}$ which explicitly take into account the presence of two different velocities $V_p$ and $V_s$.

4. The basic hypotheses concerning the transport fluxes. — The equation of conservation for the polymer mass is actually

$$\frac{\partial \rho_p}{\partial t} + V \cdot \rho_p V_p = 0.$$  

Comparing with (14) we deduce with the help of (11)

$$J = \rho_p (V_p - V) \equiv P.$$  

(22)

Moreover the conservation of momentum must certainly appear as

$$\frac{\partial \rho V}{\partial t} + V \cdot (\rho_p \overline{VV_p} + \rho_s \overline{VV_s} + p \overline{I} + \overline{\pi}^*) = \rho g$$

hence, comparing with (16) we should write

$$\overline{\pi} = \frac{p}{\rho_p} + \overline{P} + \overline{\pi}^*$$

(23)

where $\overline{\pi}^*$ is yet undetermined.

Concerning the entropy flux $S$, things are a bit more delicate. If the specific entropies $s_{p0}$ and $s_{s0}$ indeed move with $V_p$ and $V_s$ respectively it is generally difficult to decide with which velocity the entropy of mixing and the entropy of deformation are convected. But if we notice that for dilute solutions, both these entropies are proportional to $\rho_p$ (see eq. (9)) it seems reasonable to propose that in this limit they are both convected with $V_p$. Consequently, defining the effective polymer specific entropy as

$$s_p = s_{p0} - \frac{k}{m_p} \left[ \log \frac{\rho_p}{\rho_p^0} + \frac{1}{2} (C_{ij} - \delta_{ij})^2 \right]$$

(24)

we see that the total entropy flux should be written as the sum

$$\rho_p s_p V_p + \rho_s s_{s0} V_s + s = SV + (s_p - s_{s0}) P + s,$$

with $S$ defined by equation (9). Now by comparing with the left-hand side of equation (20) we deduce that

$$S = (s_p - s_{s0}) P + s.$$  

(25)

Lastly the dumbbell model [18] suggests that for a dilute solution the evolution in time of the polymer shape is

$$\frac{\partial \overline{R}}{\partial t} + (V_p \cdot V) \overline{R} = \overline{\omega}_s \overline{C} + \overline{C} \overline{\omega}_s +$$

$$+ \beta (\overline{D}_s \overline{C} + \overline{C} \overline{D}_s) - \frac{1}{\tau} (\overline{C} - \overline{T})$$

(26)

and this implies that our $\overline{R}$ in (19) is likely to take the form

$$\overline{R} = -\frac{1}{\rho_p} (P \cdot V) \overline{C} + \overline{\omega}_s \overline{C} + \overline{C} \overline{\omega}_s +$$

$$+ \beta (\overline{D}_s \overline{C} + \overline{C} \overline{D}_s) + \overline{r}$$

(27)

where $\overline{r}$ is related to the relaxation of the polymer deformation. The above equation (26) means that in the frame moving with the particle velocity and rotating with the angular velocity $\overline{\omega}_s$ of the solvent, the polymer deformation is the result of a relaxation towards the equilibrium (spherical) shape and of the action of the solvent deformation rate $\overline{D}$ (the symmetric part of the tensor $\overline{VV}$) with an efficiency coefficient $\beta$ that we expect to be in the range of zero (for rigid molecules) to one (for perfectly deformable ones) and which increases when the hydrodynamic interaction between the monomers decreases [19].
5. The entropy production (second stage). — Taking into account the following identity

\[
\nabla \cdot \dot{V} = \nabla \cdot (P/\rho) \simeq \nabla \cdot V - \frac{1}{\rho} \nabla \cdot P,
\]

(the last equality is valid for dilute solutions only) we finally transform equation (20) with the help of equations (22), (23), (25) and (27) into

\[
\frac{\partial S}{\partial t} + \nabla \cdot (SV + S) = - \frac{1}{T} [s_* \nabla T + f_* \nabla + \tilde{r} \cdot \nabla + \tilde{r} \cdot \tilde{S}] \tag{28}
\]

where the final fluxes appearing in the entropy balance are related to the former ones appearing in equations (14) to (19) by the following relations (some of which were already stated)

\[
\begin{align*}
J &= P \\
S &= (s_p - s_o) P + s \\
\overline{R} &= - \frac{1}{\rho_p} (P \cdot \nabla) C + \omega_a \cdot \overline{C} + \frac{1}{\rho_a} \omega_a + \\
+ \beta (C \cdot \overline{D} + \overline{D} \cdot C) + \tilde{r} \\
\overline{\pi} &= \frac{p \overline{T} + \overline{F} - \beta (\overline{a} \cdot \overline{C} + \overline{C} \cdot \overline{\alpha}) + \tilde{r}}{\rho} \\
\overline{T} &= \frac{1}{\rho} (\overline{a} \cdot \overline{C} + \overline{C} \cdot \overline{\alpha}) + \tilde{r} \\
F &= - (s_p - s_o) \nabla T - \nabla (\mu_p - \mu_s) + \frac{1}{\rho_p} \alpha_{ij} VC_{ij} - \\
- (w \cdot \nabla) V + f \tag{31}
\end{align*}
\]

while the energy flux is given by

\[
Q = TS + (\mu_p - \mu_s) J + P \cdot \overline{T}. \tag{21}
\]

The main result of this section is represented by the expressions (30) and (31) for \( \overline{T} \) and \( F \) (1). We have just shown how these terms entering the relative velocity equation of motion (18) may be obtained unambiguously provided the relative velocity dependence of the fluxes \( S, J, \overline{\pi} \) and \( \overline{R} \) is known or at least guessed at. It must be stressed that other choices are possible. One may claim for instance that the entropy of mixing and the entropy of deformation are convected with the centre of mass velocity \( V \), and also that the polymer shape depends on \( \overline{a} \) and \( \overline{D} \) (the components of \( \overline{V} \)) instead of \( \omega_a \) and \( \overline{D} \). In this case we would have found with the same procedure

\[
\frac{\partial S}{\partial t} + \nabla \cdot (SV + S) = - \frac{1}{T} [s_* \nabla T + f_* \cdot \nabla + \tilde{r} \cdot \nabla + \tilde{r} \cdot \tilde{S}] \tag{32}
\]

(1) The expression (29) for \( \overline{\pi} \) is also of utmost importance but its implications were already analysed in [20].
equation (18) can be transformed into
\[ \frac{D_p V_p}{Dt} - \frac{D_v V_v}{Dt} + \left( \frac{1}{\rho_p^0} - \frac{1}{\rho_s^0} \right) V_p = \]
\[ = - \frac{kT V_p}{\rho_p} - V_v \left[ \frac{\beta}{\rho} (\bar{\alpha}.\bar{C} + \bar{\Xi}.\bar{Z}) \right] + f - V.\bar{v} \]
(36)
with the hypothesis leading to equations (30) and (31),
or into
\[ \frac{D_p V_p}{Dt} - \frac{D_v V_v}{Dt} + \left( \frac{1}{\rho_p^0} - \frac{1}{\rho_s^0} \right) V_p = \]
\[ = - V(\Delta \mu_p) + f^* - V.\bar{v} \]
(37)
with the hypothesis leading to equations (33) and (34)
(the expression for V(\Delta \mu_p) is given by Eq. (35)).
Expressions (36) and (37) are the central results of
this paper and we end this section with the expressions
for f (or f*) and \( \bar{v} \) (or \( \bar{v}^* \)). From either of the entropy
production equations (28) or (32), we deduce that
\[ f = - \frac{v_1}{\rho_p^0 r_0^2} \rho_p \]
and
\[ \bar{v}^* = - \frac{v_3}{\rho_p^0} \frac{V_p}{V_v} - v_3 \frac{V_v}{V_v} \]
where the \( v_k \) are kinematic viscosities with \( v_1 \) and \( v_2 \)
positive scalars while the sign of \( v_3 \) is arbitrary (the
other terms like \( \rho_p^0 \) and \( r_0 \) are introduced for dimen-
sional convenience only). For a dilute solution
\[ V \approx V_s \text{ and } \rho \approx \rho(V - V_s) \]
and in this approximation
\[ f - V.\bar{v} = - \frac{v_1}{\rho_p^0 r_0^2} \rho_p + v_3 V_v V_s. \]
This result must be compared with the viscous force \( F_v \)
acting on a particle in an arbitrary velocity field, the
so-called Faxen's force [12]
\[ F_v = - \zeta \left( V_p - V_s - \frac{r_0^2}{6} \nabla^2 V_v \right) \]
(38)
where
\[ \zeta = 6 \pi \eta_s r_0 \]
is the friction coefficient and \( \eta_s \) the solvent viscosity.
It is not difficult to convince oneself that for a dilute solution
\[ f - V.\bar{v} = F_v/m_p = f^* - V.\bar{v}^* \]
(40)
where \( m_p \) is the polymer mass and consequently
\[ v_1 = \frac{1}{\rho_p} \frac{\xi \rho_p^0 r_0^2}{m_p} \approx \frac{9}{2} \frac{\eta_s}{\rho_p}, \]
and
\[ v_3 = \frac{3}{4} \frac{\eta_s}{\rho_p}. \]
We shall not bother further with the exact values of \( v_1 \) and \( v_3 \) and, instead, we shall consider henceforth
that in both equations (36) and (37), the viscous force
\[ f - V.\bar{v} \text{ or } f^* - V.\bar{v}^* \]
is given by equation (40) where \( F_v \) is the Faxen's
force (38).

7. Comparison with previous work. — 7.1 The
entropic force scheme. — If we consider a neutrally-
buoyant mixture (\( \rho_p^0 = \rho_o^0 \)) in a stationary motion
with negligible acceleration
\[ \frac{D_p V_p}{Dt} = \frac{D_v V_v}{Dt} \approx 0 \]
then from equations (37) and (40) we get
\[ F_v/m_p = V(\Delta \mu_p) \]
(41)
and
\[ \bar{V}(\Delta \mu_p) + f* - V.\bar{v}^* \]
where \( V(\Delta \mu_p) \) and \( F_v \) respectively given by equations (35)
and (38). The resulting expression for the diffusion
mass flux \( J \) is thus
\[ J = \rho_p (V_p - V_s) \]
\[ = \rho_p \frac{r_0^2}{6} \nabla^2 V_s - \frac{kT}{\zeta} \left[ \rho_p \rho_p + m_p \alpha_{ij} V C_{ij} \right. \]
\[ - \left. \frac{\rho_p m_p}{kT} \left( \rho_o^0 - \rho_o^0 \right) \nabla^2 T \right] \]
(42)
where \( \alpha_{ij} \) is given by (10). Except for the terms involving
\( \nabla^2 V_s \) and \( \nabla^2 T \); the above expression is exactly the one
found by Tirrell and Malone [14]. The name entropic
force comes from the shape dependence of the chemical
potential which is mainly entropic in origin.

7.2 The SAJ force scheme. — Again for neutrally-
buoyant mixtures and negligibly accelerated flows,
equations (36) with (40) merges into
\[ F_v/m_p = \frac{kT}{\rho_p} V \]
\[ + \left[ \frac{\beta}{\rho_p^0} (\bar{\alpha}.\bar{C} + \bar{\Xi}.\bar{Z}) \right] \]
(43)
and the diffusion mass flux is in this case
\[ J = \rho_p \frac{r_0^2}{6} \nabla^2 V_s - \]
\[ - \frac{kT}{\zeta} \left[ \nabla \rho_p + \frac{m_p \rho_p}{kT} \nabla \left[ \frac{\beta}{\rho_p^0} (\bar{\alpha}.\bar{C} + \bar{\Xi}.\bar{Z}) \right] \right]. \]
(44)
Note the quite different structure between (42) and
(44), in particular the presence of \( \bar{\alpha} \) inside a divergence
term in (44). As a consequence, expression (44) is
likely to include anisotropic terms involving \( \nabla \rho_p \).
and $\mathbf{vT}$ (due to the $\rho_p$ and $T$ dependence of $\bar{V}$ see eq. (10)) while such a possibility is excluded from (42). Moreover the part of (42) depending on the polymer shape $\bar{C}$ only implies a cross-streamlines migration (see ref. [14]) while the more complicated structure of the corresponding part of (44) is compatible with cross-streamlines as well as along-streamlines migration, as we shall later see. The structure of expression (44) thus bears many resemblances to that deduced by Sekhon, Armstrong and Jones from a kinetic theory approach [13] but the physical interpretation of this part of the mass flux depending on the polymer deformation needs some clarification.

8. Re-interpretation of the SAJ-like force. — Let us consider the relative position vector $\mathbf{r}$ separating the centres of two spheres submitted to a non-uniform velocity field with a rotation vector $\mathbf{\Omega}$ and a gradient of strain rate $\mathbf{\nabla}$. If the two spheres interact via a force $\mathbf{F}$ (including the Brownian motion force) we can write with Batchelor [21, 22]

$$\frac{d\mathbf{r}}{dt} = \bar{\Omega} \times \mathbf{r} + \mathbf{\nabla} \cdot \mathbf{r} - \left\{ \frac{A(r) \bar{\Omega}^2}{r^2} + B(r) \left( \bar{t} - \frac{\bar{\Omega}^2}{r^2} \right) \right\} \cdot \mathbf{\nabla} \cdot \mathbf{r} + \frac{1}{\zeta} \left\{ \frac{G(r) \bar{\Omega}^2}{r^2} + H(r) \left( \bar{t} - \frac{\bar{\Omega}^2}{r^2} \right) \right\} \mathbf{F}. \quad (45)$$

In the dumbbell model, the polymer molecule is compared to such a system of two interacting spheres and $\mathbf{r}$ now represents the deformation of the molecule. In their dumbbell model approach to the diffusion flux, Sekhon, Armstrong and Jones [13] emphasized on the role of the hydrodynamic interactions in the anisotropic nature of the diffusion tensor, i.e. on the terms $G$ and $H$ of the above equation. But hydrodynamic interactions have another role which is the modification of the effective velocity field seen by each monomer due to the presence of other monomers and this is represented by the terms $A$ and $B$ of the above equation. When statistically averaging equation (45) to get an equation like (26) for $C_{ij} = 3 < r_i r_j >/r_0^2$, the role of the anisotropic diffusion tensor is merely to renormalize the relaxation time for the polymer deformation [18], while the role of $A(r)$ and $B(r)$ is to appear as the coefficient $\beta$ in equation (26), this coefficient playing a crucial role in the expression (44) of the diffusion flux. Thus, if the SAJ force had indeed something to do with hydrodynamic interactions inside a polymer molecule, we have the feeling that the modification of the effective velocity field is far more important than the anisotropy of the diffusion tensor.

9. Migration in a Poiseuille flow. — Let us consider a Poiseuille flow with the simple velocity field $V_z(r)$ for the solvent. The shape of the polymer molecule is given by the solution of equation (26) which is

$$C_{rr} = [1 + (1 - \beta) X^2]^{-1}, \quad C_{zz} = [1 + (1 + \beta) X^2]^{-1}, \quad C_{rz} = \beta X [1 + (1 - \beta) X^2]^{-1}, \quad C_{\theta\theta} = C_{\phi\phi} = 0, \quad C_{\theta\phi} = 1.$$

where $X(r)$ is the Deborah number

$$X = \tau \frac{dV_z}{dr} \quad (46)$$

while $\tau$ is the Zimm relaxation time. Note that, except for the case $\beta = 1$ corresponding to the absence of hydrodynamic interactions, the polymer shape is always finite whatever the Deborah number is. With $\bar{V}$ given by equation (10), we are then able to express the diffusion mass flux as a function of $V_z$ and its spatial derivatives, using either equation (42) or equation (44). If we are confident that equation (42) is the right answer we get for isothermal Poiseuille flow

$$J_z = \rho_p \frac{r_0^2}{6} \frac{1}{r} \frac{d}{dr} \left( r \frac{dV_z}{dr} \right), \quad J_r = -\frac{kT}{\zeta} \left[ \frac{d\rho_p}{dr} + \rho_p (C_{rr} - 1) \frac{dC_{rr}}{dr} + \rho_p (C_{zz} - 1) \frac{dC_{zz}}{dr} + \rho_p C_{rz} \frac{dC_{rz}}{dr} \right], \quad J_\theta = 0 \quad (47)$$

but if we prefer equation (44) we get again for an isothermal flow with $\beta$ and $\rho_p^0$ taken as constants,

$$J_z = \rho_p \frac{r_0^2}{6} \frac{1}{r} \frac{d}{dr} \left( r \frac{dV_z}{dr} \right) - \frac{kT}{\zeta} \frac{2 \beta \rho_p}{\rho_p^0} \frac{1}{r} \frac{d}{dr} \left[ \rho_p \frac{C_{rz} (C_{rr} + C_{zz} - 1)}{r \frac{dC_{rr}}{dr}} \right], \quad J_r = -\frac{kT}{\zeta} \left[ \frac{d\rho_p}{dr} + \frac{2 \beta \rho_p}{\rho_p^0} \frac{1}{r} \frac{d}{dr} \left[ \rho_p (C_{rz} + C_{zz} - C_{rr}) \right] \right], \quad J_\theta = 0.$$
If we express the components $C_{ij}$ as a function of the Deborah number, the resulting expressions are very complicated. For this reason we limit ourselves to the low Deborah number limit ($\chi \ll 1$) and the cross-streamlines component of $J$ is in this case

$$J_r = -\frac{kT}{\zeta} \left[ \frac{d\rho_p}{dr} + \rho_p \beta^2 \tau^2 \frac{dV}{dr} \frac{d^2V}{dr^2} \right]$$  \hspace{1cm} (49)

or

$$J_r = -\frac{kT}{\zeta} \left\{ \frac{d\rho_p}{dr} + \frac{2 \beta \rho_p}{\rho_p^0} (2 \beta - 1) \tau^2 \frac{1}{r} \frac{d}{dr} \left[ r \rho_p \left( \frac{dV}{dr} \right)^2 \right] \right\}$$  \hspace{1cm} (50)

depending on which expression for $J$ we take for granted. Anyway the above expressions confirm the existence of an anisotropic diffusion in the SAJ force scheme (expressed by the presence of $d\rho_p/dr$ in $J_r$), and a much weaker effect (of the order $2 \beta \rho_p/\rho_p^0$) of the cross-streamlines diffusion with the SAJ force (eq. (50)) as compared to the entropic force (eq. (49)).

10. The Soret effect. — The diffusion mass flux depends on the temperature gradient. This is clearly seen in (42) and the Soret coefficient is in this case the sum of two terms, one of them depending on the polymer deformation as is apparent from inspection of equation (24). For the case of the SAJ force and the corresponding diffusion flux (44), the temperature gradient is implicitly present through the temperature dependence of $\overline{a}$ (see eq. (10)) and the remarkable fact is that the Soret coefficient is now proportional to the particle deformation and is thus likely to be unobservable at low Deborah numbers.

11. Conclusion. — We have shown that the well-known entropic force or the more recent SAJ force can both be justified depending on the hypothesis made concerning the entropy transport and the dynamics of the polymer deformation. If the deformation entropy of the polymer molecules and the entropy of mixing are both convected with the centre of mass velocity $V$, and if the polymer shape is influenced by the gradient of $V$, then our thermodynamic analysis shows that for non-accelerated flow of a neutrally-buoyant mixture, the mass flux is given by the gradient of a chemical potential, as in the case for the Fick’s law. But if we adopt the (more plausible) hypothesis that both extra entropies are convected with the polymer velocity and that the polymer shape is mainly dependent on the gradient of the solvent velocity, then we get for the diffusion mass flux an expression which is rather similar to that found through a kinetic theory approach by SAJ [13]. Moreover it happens that the Soret coefficient crucially depends on the molecular shape for this last case while only a part of this coefficient is shape dependent in the former case. Lastly the part of the diffusion mass flux depending on the polymer shape is less by a factor $\beta \rho_p/\rho_p^0$ (i.e. $\beta$ times the polymer volumic fraction) in the case of the SAJ force compared to the case of the entropic force. Thus the expected effects on migration are generally weaker with the SAJ force.

References