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Non-equilibrium chemical potential and polymer extraction from a porous matrix

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Abstract

The influence of a flow on the transfer of a polymer solution from a porous matrix to a flowing fluid is analysed. Since the flow modifies the free energy of the solution, through stretching and orientation of the macromolecules, the thermodynamic driving force for polymer transport is modified with respect to that of a quiescent fluid. The consequences of this modification for the extraction of a polymer from a porous matrix are explored in detail, and the formal results are explicitly illustrated by means of a specific solution. For the particular example analysed here, of possible interest in oil extraction or in microfluidic problems, the non-equilibrium effects may yield a reduction of the order of 10% of the extraction rate.

Keywords: Chemical potential; Polymer solutions; Non-equilibrium thermodynamics

1. Introduction

Polymer extraction from a porous matrix is a problem of much practical interest as, for instance, in oil extraction or pollutant extraction from a soil, or in chromatographic techniques, which have received a recent impulse from microfluidics and nanofluidics situations. From a detailed, fundamental point of view, one of the questions arising in this situation is the expression for the thermodynamic force driving the polymer from the porous matrix to the fluid along a channel drilled in the matrix, which is the free energy difference between the polymer in the pores and in the fluid (the situation is sketched in Fig. 1). Both the enthalpy and the entropy play thus a role in this process. Recently, in order to study the effects of entropic barriers on polymer motion, the role of the entropy difference between a polymer placed in two neighbouring regions has been discussed by several authors [1–4]. Application of these ideas to a practical situation as polymer extraction seems an interesting topic for both non-equilibrium thermodynamics and rheology.

When flowing from the porous medium to the bulk fluid, the entropy of the polymer will be much higher in the latter than in the channels of the former, because a much higher number of microscopic configurations will be accessible for it in the fluid. Usually, it is assumed that the motion of the fluid where the polymer is going does not contribute to the free energy. However, if the fluid is in motion along a channel (much wider than the pores but sufficiently narrow to have a relevant velocity gradient) the polymer will be elongated and oriented by the flow, thus increasing its internal energy and reducing its entropy with respect to its corresponding value in the fluid at rest. This will have an influence both on the entropy barrier as well as for the entropy difference between the initial (porous matrix) and the final (free fluid) states of the polymer.

In this paper, we want to take into account the flow contribution to the free energy of the polymer in the fluid and, consequently, on the thermodynamic force driving the transport of the polymer from the porous matrix to the fluid. These effects may be relevant in the practical extraction of polymers from a porous matrix, in situations when relatively

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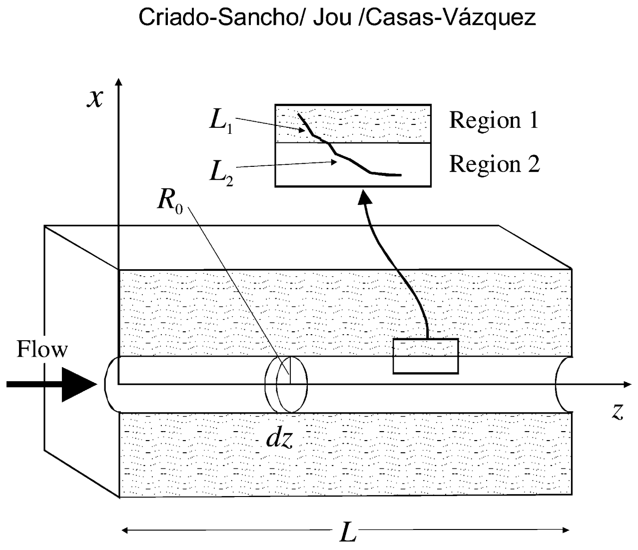

Fig. 1. Sketch of the situation considered in this paper. Polymers embedded in the porous region are extracted from it by means of a flow of a suitable solvent flowing along a cylindrical tube drilled in it.

narrow channels are drilled into the porous matrix and a solvent is made to flow along them. In Section 2 the flow contribution to the polymer free energy is examined and the equations describing its transfer from the matrix to the fluid in the channel are settled. In Section 3, an explicit analysis of the influence of the non-equilibrium contribution is carried out, and finally, in Section 4, the results are discussed.

2. Flow contribution to the polymer free energy

In the simplest situation, one may consider the polymer as a freely-jointed chain constituted by N monomers of length b. The corresponding free energy of a polymer solution with n chains per unit volume at temperature T in a fluid under a shear viscous pressure $\mathbf{P}^{\mathrm{v}}$ is [5,6].

$$F(T,n,\mathbf{P}^{\mathrm{v}}) = \text{constant} + \frac{3nk_{\mathrm{B}}T}{2Nb^2}\langle\mathbf{R}^2\rangle_{\mathrm{eq}} + \frac{J}{4}\mathbf{P}^{\mathrm{v}}:\mathbf{P}^{\mathrm{v}} \tag{1}$$

where k_{B} is the Boltzmann constant and $\langle\mathbf{R}^2\rangle$ the average of the square of the end-to-end vector $\mathbf{R}$. In a quiescent fluid, this average is $\langle\mathbf{R}^2\rangle_{\mathrm{eq}}$, but in the presence of a flow characterized by the viscous pressure tensor $\mathbf{P}^{\mathrm{v}}$, $\langle\mathbf{R}^2\rangle$ is modified. This modification is accounted for by the last term on the right-hand side, where J is the steady-state compliance. In previous analyses [7–11], we have studied widely the influence of this term—with more refined expressions for dilute, semidilute and entangled solutions—in shear-induced diffusion, in the shear-induced shift of the spinodal line of flowing polymer solutions and in shear-induced concentration banding. All of them are topics, which are focusing much recent attention [7,12–14].

The use of the viscous pressure as independent variables is typical of the so-called extended irreversible thermodynamics [15,16] but other approaches to the influence of the flow on the polymer solutions may be found, for instance, in [14,17–20], where the macromolecular configuration tensor is taken as an independent variable instead of the viscous pressure tensor. In the linear approximation, both tensors are proportional to each other and it is possible to go directly from the description based on the viscous pressure tensor to that based on the configuration tensor.

Here, to be specific, we will consider a simple explicit situation, in which a cylindrical channel of radius R_0 and length L has been drilled along the z-axis inside a porous matrix of infinite extension in the x–z directions. We will study the influence of the non-equilibrium term on the quantity of practical interest, namely, the mass of polymer extracted from the matrix per unit time

$$\frac{\mathrm{d}w}{\mathrm{d}t} \equiv \frac{\text{mass of polymer extracted}}{\text{time}} \tag{2}$$

This quantity will be given, in the simplest situation, by

$$\frac{\mathrm{d}w}{\mathrm{d}t} = c(L)Q \tag{3}$$

where Q is the flow rate along the cylindrical channel and $c(L)$ is the average concentration of the polymer in the outgoing solution. Such a quantity will depend on the driving force, namely, the difference of chemical potential of the polymer in the flowing fluid μ and in the porous matrix μ_1, and on the lateral area of the channel.

To obtain $c(L)$ one needs to know the profile $c(z)$ of the average polymer concentration along the tube. From now on we will restrict ourselves to an average concentration across each transversal section of the tube; in fact, the exploration of the transverse concentration profile as a function $c(z,r)$, both in the radius and the longitudinal position would be of interest, but for our purposes here the average density is sufficient. The equation governing the longitudinal concentration profile is given by a combination of the mass conservation equation and a phenomenological equation for the polymer transfer across the surface between the porous medium and the flowing fluid.

We assume that the rate of polymer transfer per unit surface of the channel wall is given by

$$J_{\mathrm{p}} = \alpha[\mu_1(T,c_1) - \mu(T,c,P_{rz}^{\mathrm{v}})] \tag{4}$$

where c_1 is an effective concentration of polymer in the porous matrix, P_{rz}^{v} the viscous pressure acting on the fluid, and α a phenomenological coefficient (whose microscopic meaning will be discussed in Section 4) describing the transfer of the polymer between both media per unit area and time. One of the new aspects of the present paper is to take into consideration the fact that the flow may contribute to the chemical potential in the fluid in such a manner than the latter adopts the form

$$\mu(T,c,P_{rz}^{\mathrm{v}}) = \mu_{\mathrm{eq}}(T,c) + \mu_{\mathrm{flow}}(T,c,P_{rz}^{\mathrm{v}}) \tag{5}$$

instead of the classical local-equilibrium expression μ_{eq} (T,c).

If the phenomenological transport Eq. (4) is combined with the mass conservation equation, one gets

$$Q\frac{dc}{dz} = 2\pi R_0 \alpha\{\mu_1(c_1) - \mu[c(z), P^{v}_{rz}]\} \tag{6}$$

Indeed, to obtain this expression we have equated the polymer inflow from the porous matrix across the lateral walls, $2\pi R_0 J_p dz$, to the increase in the axial flow of polymer through the transversal sections of the tube in z and $z+dz$, namely

$$c(z+dz)Q - c(z)Q \approx \left(\frac{dc}{dz}\right)Q dz \tag{7}$$

Here, we will take a more detailed perspective, to explore the role of the flow contribution to the chemical potential. As a simplifying hypothesis it is assumed that equilibrium chemical potential expression has the same form in both regions; this is not necessarily true, because of the presence of the solid matrix in the porous region. Nevertheless, as in our previous works [7,10,11,21] we will take for the equilibrium chemical potential of the polymer in the fluid the Flory–Huggins expression

$$\frac{\mu_{FH}}{RT} = \ln\phi + (1-N)(1-\phi) + \chi N(1-\phi)^2 \tag{8}$$

where the volume fraction ϕ and the concentration c are related by $\phi = v_1 Nc/M_2$, being v_1 the solvent molar volume and M_2 the molecular mass of the polymer and χ the interaction parameter. As an additional hypothesis, we also assume effective values of the interaction parameter and concentration for the porous region (χ_1 and c_1, respectively), which are in principle different from the interaction parameter χ in the fluid.

Using the auxiliary quantities

$$\tilde{z} = \frac{z}{L}, \quad \tilde{c} = [\eta]c, \quad Q_0 = \frac{Q}{R_0^3}, \quad \tilde{w} = \frac{[\eta]w}{R_0^3} \tag{9}$$

with $[\eta]$ the intrinsic viscosity, Eq. (6) can be written in a compact form as

$$\frac{d\tilde{c}}{d\tilde{z}} = \frac{\lambda\alpha_0}{Q_0}\left[\frac{\mu_{FH}(\tilde{c}_1,\chi_1)}{RT} - \frac{\mu_{FH}(\tilde{c},\chi)}{RT} - \frac{\mu_{flow}(\tilde{c},P^{v}_{rz})}{RT}\right] \tag{10}$$

being λ and α_0 the new coefficients

$$\lambda = \frac{L}{R_0}, \quad \alpha_0 = \frac{2\pi[\eta]RT}{R_0}\alpha \tag{11}$$

and R the gas constant. Note that in this notation, Eq. (3) takes the form

$$\frac{d\tilde{w}}{dt} = \tilde{c}(1)Q_0 \tag{12}$$

As for the flow contribution to the chemical potential namely, the second term on the right-hand side in (5), the following expression [21] is taken, which is based on extended irreversible thermodynamics [7,16].

$$\frac{\mu_{flow}}{RT} = \frac{Cv_1M_2[\eta]}{4R^2T^2}\left[\frac{M_2[\eta]}{v_1}\frac{\Phi(\tilde{c})}{\tilde{c}} + 2\left(\frac{M_2[\eta]}{v_1\tilde{c}} - N\right)\frac{P_5(\tilde{c})}{P_6(\tilde{c})}\right]\langle \mathbf{P}^{v} : \mathbf{P}^{v}\rangle \tag{13}$$

where the transversal average $\langle \mathbf{P}^{v}:\mathbf{P}^{v}\rangle$ is taken in order to avoid the existence of a radial profile of viscous pressure along the tube, consistently with our focusing on the average polymer concentration. Notice that Eq. (13), which is valid for more general models than the freely-connected chain, is obtained by differentiation of the flow contribution to the free energy [7,16] $\Delta G_{flow} = 1/4\, JV\, \mathbf{P}^{v}:\mathbf{P}^{v}$ with respect to the number of moles of solute.

For dilute or semidilute solutions, for which Zimm and Rouse models for polymers can be, respectively, applied, J takes the form [5,7]

$$J = \frac{CM_2}{cRT}\left(1 - \frac{\eta_s}{\eta}\right)^2 \tag{14}$$

where $C=0.4$ is the Rouse constant and $C=0.206$ the Zimm constant, M_2 the molecular mass of the polymer and η_s is the viscosity of the pure solvent. We also assumed a viscosity dependence on concentration given by

$$\eta(\tilde{c}) = \eta_s(1 + \tilde{c} + k\tilde{c}^2) \tag{15}$$

where k stands for the Huggins constant.

If for the sake of simplicity we assume that the flowing solution behaves as a Newtonian fluid, it can be shown that the average of the square of the viscous pressure is given by

$$\langle \mathbf{P}^{v} : \mathbf{P}^{v}\rangle = \frac{16Q_0^2}{\pi^2}\eta^2(\tilde{c}) \tag{16}$$

This average corresponds to the typical parabolic velocity profile in Poiseuille flow. Note, however, that we assume that the viscosity of the solution will be in principle a function of the polymer concentration $\eta(\tilde{c})$, which is a realistic assumption.

An especially simple version of equation $c(z)$ is obtained when we assume that $\mathbf{P}^{v}$ does not influence the chemical potential and $\chi_1 \approx \chi$, then

$$\mu_{FH}(\tilde{c}_1) - \mu_{FH}(\tilde{c}) = \left(\frac{\partial\mu_{FH}}{\partial\tilde{c}}\right)_{\tilde{c}_1}(\tilde{c}_1 - \tilde{c}) \tag{17}$$

In this case, Eq. (10) simplifies to

$$\frac{d\tilde{c}}{d\tilde{z}} = \frac{\lambda\alpha_0^0}{Q_0}(\tilde{c}_1 - \tilde{c}) \tag{18}$$

where α_0^0 is given by $\alpha_0^0 = (\alpha_0/RT)(\partial\mu_{FH}/\partial\tilde{c})_{\tilde{c}_1}$. Integration of (18) lets us write for the reduced concentration profile

$$\tilde{c} = \tilde{c}_1\left[1 - \exp\left(-\frac{\lambda\alpha_0^0}{Q_0}\tilde{z}\right)\right] \tag{19}$$

from which Eq. (3) takes the form

$$\frac{\mathrm{d}\tilde{w}}{\mathrm{d}t} = Q_0\tilde{c}_1\left[1-\exp\left(-\frac{\lambda\alpha_0^0}{Q_0}\right)\right] \qquad (20)$$

In Section 3, we compare the results obtained from the simple local-equilibrium Eq. (18) with the result obtained from (10), incorporating the influence of the flow on the chemical potential. In particular, we make this comparison for a particular polymer solution.

3. Explicit solution and application to polymer extraction

To be explicit, in this section we will consider polymer extraction by working with a specific polymer solution, namely, polystyrene in transdecalin, for which most of the necessary parameters are known [7,21]. Of course, the analysis would be of higher practical interest if oil was considered, but we do not know, at present, the necessary parameters.

In Figs. 2 and 3 the longitudinal concentration profile along the tube is plotted as a function of the longitudinal position. Solid lines refer to the results of the full Eq. (10), incorporating the effects of the non-equilibrium chemical potential, whereas dashed lines correspond to the simple exponential profile (19), where such effects where not incorporated. Figs. 2 and 3 correspond to different values of the coefficient $\alpha_0\lambda$ (namely, 0.5, corresponding to a short tube or to a low exchange coefficient for the polymer between the soil and the tube, and 10, namely, a longer tube or a higher exchange coefficient). In both cases, the profiles are obtained for different values of $Q_0 \equiv Q/R^3$. The gross features of the profiles are as expected: Of course, they increase with z and, furthermore, for a given z they decrease with the flow rate. The latter feature, though less obvious than the first one, was expected, too, because the higher the value of Q the farther will be the system from equilibrium and the lower will be the concentration $c(z)$ at any value of z along the tube.

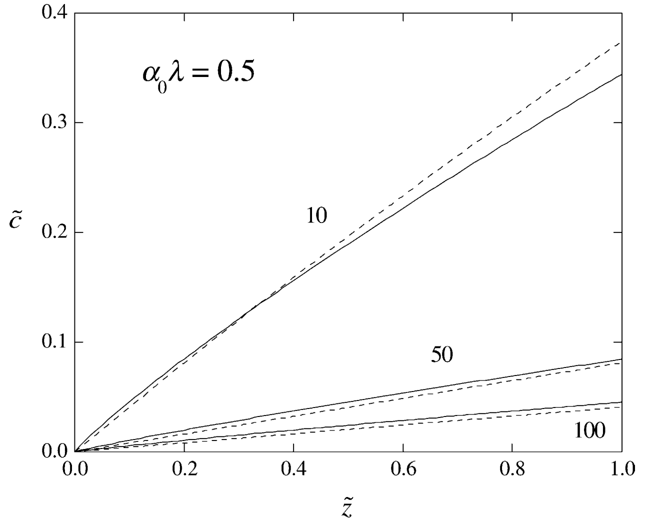

Fig. 2. Reduced concentration profile along the tube for $\alpha_0\lambda = 0.5$ for several values of the reduced flow rate. The dashed line corresponds to the classical approximation, in which the flow contributions to the chemical potential of the polymer are neglected, whereas the solid line takes them into account.

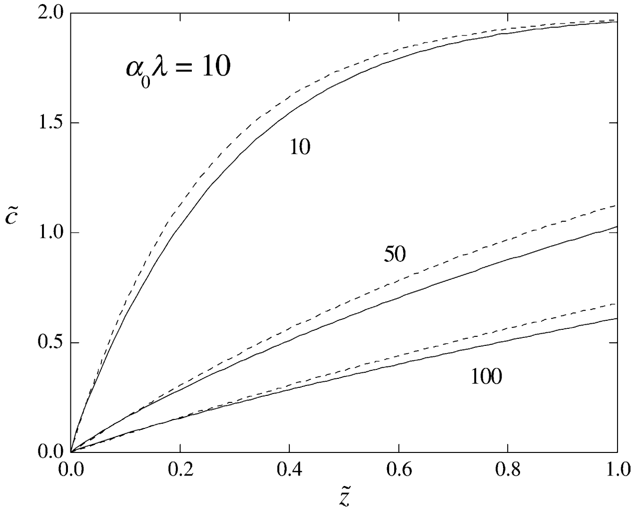

Fig. 3. The same of Fig. 2 for $\alpha_0\lambda = 10$.

The original aspect of our work is to study the influence of the non-equilibrium contribution of the flow to the chemical potential of the polymer on the extraction features. This is mainly reflected in the comparison of the full lines (including this feature) and discontinuous lines (the simplest model). In principle, one should naively expect that the concentration in the tube would be less when the flow contribution is included, because in this case the free energy of the polymer on the flowing fluid is higher than in the case when the flow contribution is ignored, and, as a consequence, the thermodynamic force driving the polymer transfer from the soil to the tube will be less than in usual circumstances. This is indeed found in all the lines of Fig. 3 and in the higher line in Fig. 2. However, this is not so for the two lower curves in Fig. 2, namely, for high values of the flow. This is due because these curves correspond to a low concentration; a detailed analysis shows that, due to the non-monotonic dependence of the non-equilibrium contribution ΔG_{flow} on the concentration, the flow contributions to the chemical potential are negative for low densities, this raising the transport from the porous medium to the fluid, and they are positive for high densities, thus reducing such a transport.

Concerning the rate of extraction $\mathrm{d}\tilde{w}/\mathrm{d}t$ as a function of the reduced flow rate Q_0, it is plotted in Figs. 4 and 5 for different values of the coefficient $\alpha_0\lambda$. Solid lines refer to the full situation and dashed lines correspond to the classical situation. In Fig. 4, it is seen that the non-equilibrium effects lower the extraction rate, in 12 and 10% approximately for $\alpha_0\lambda = 10$ and $\alpha_0\lambda = 5$, respectively. In contrast, for small

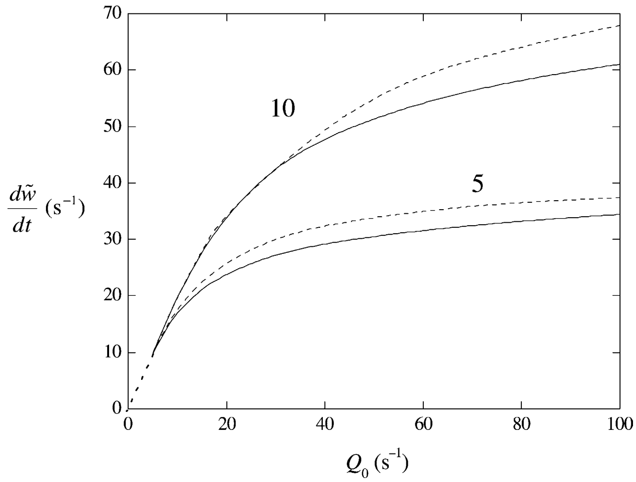

Fig. 4. Polymer extraction rate (in reduced units) as a function of the reduced flow rate of the fluid, for $\alpha_0\lambda=5$ and $\alpha_0\lambda=10$. The dashed line corresponds to the classical approximation in which the flow contributions to the chemical potential of the polymer are neglected, whereas the solid line takes them into account.

values of $\alpha_0\lambda$ and for high enough values of Q_0, Fig. 5 shows a small enhancement of the extraction rate with respect to the classical prediction. This is due because in this situation the concentration is usually small, and the flow contribution to the chemical potential is negative, as we have commented above. In fact, the value of Q_0 for which the extraction rate in the full non-equilibrium model becomes higher than in the classical model, let us denote it as Q_0', increases with the parameter $\alpha_0\lambda$ (in fact, it increases as $Q_0' \approx 60\alpha_0\lambda$); thus, for high values of $\alpha_0\lambda$ corresponding to Fig. 4, all the values of Q_0 considered in the figure are below this crossover value and, correspondingly, the classical value is above the general non-equilibrium value.

The fact that the non-equilibrium effects are especially important for high values of $\alpha_0\lambda$ is easy to understand from a qualitative point of view. Indeed, high values of λ for given values of Q_0 and of the tube length L, correspond to narrow channels, where the velocity gradients will be higher and, therefore, its stretching and ordering influence will be higher and so will be non-equilibrium effects. This is also the case of parameter α_0, which is inversely proportional to the radius of the channel.

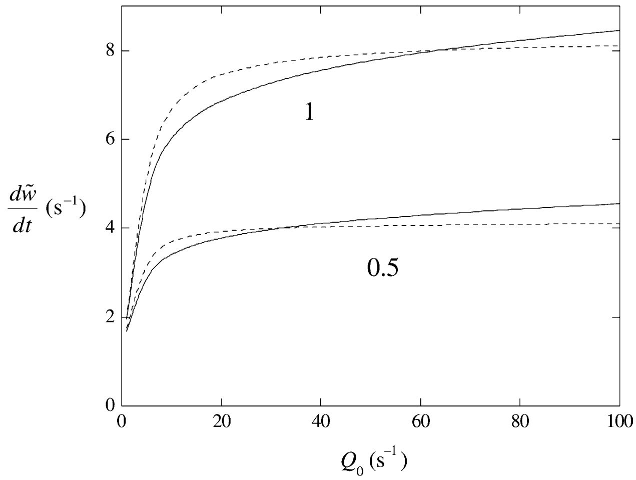

Fig. 5. The same of Fig. 4 for $\alpha_0\lambda=0.5$ and $\alpha_0\lambda=1$.

4. Concluding remarks

Before concluding this paper, it is interesting to discuss from a microscopic point of view the transport coefficient α used in Eq. (4) to describe the polymer transport from the porous matrix to the fluid. Now we will give a simple microscopic interpretation, by following the general lines suggested in [1]. Assume that the polymer concentration in the porous matrix is c_1. The polymer molecules will escape from the matrix to the fluid, driven by the entropy increase they find in the fluid. The polymer flow per unit area and time will be

$$J_p = \alpha c_1 = \bar{v} c_1 \tag{21}$$

where $\bar{v}$ is the average velocity of the outgoing polymer. We will consider that they have a length L_2 on side 2 and a length L_1 on the porous matrix (Fig. 1). The velocity of a chain may be obtained by equation of the driving force, namely $f=-(\partial F/\partial L_1)=T(\partial S/L_1)$ to the friction force, namely,$f=\varsigma bN_1 v$, ς being the friction coefficient on one monomer and b the length of a monomer. Equating both expressions one finds

$$\bar{v} = \frac{1}{bN}\int_b^{Nb} v(\ell)\mathrm{d}\ell = \frac{1}{bN}\int_b^{Nb} \frac{T\Delta s}{\varsigma \ell}\mathrm{d}\ell = \frac{T\Delta s}{\varsigma bN}\ln N \tag{22}$$

Here, $\Delta s \equiv s_1 - s_2$ is the entropy difference of a monomer in the fluid and in the porous matrix. This term gives us a microscopic interpretation of the transport coefficient. Furthermore, this indicates that, in principle, the flow could affect not only the expression of the chemical potential considered in the previous sections, but also the transport coefficient describing the kinetics of the exchange. A more complete analysis of the situation, thus, would be achieved by assuming that α itself may be a function of the flow rate. We will not undertake this analysis here.

In summary, we have studied the transfer of polymers from a porous matrix to a flowing fluid solvent, in contrast to previous papers [1,2] considering the transfer to a quiescent fluid. We have emphasized the flow contributions to the free energy of the polymer solution and, therefore, to the thermodynamic force driving the polymer from the porous matrix to the flowing fluid, which, in the situations considered, may yield a reduction of even a 10 or 12%. Considering the effects of the fluid flow is especially realistic in some situations as for instance the analysis of polymer extraction from a porous matrix (let us say oil from some porous matrix).

To check the predictions in a detailed quantitative way would require in principle to know the concentration of the polymer in the soil and the porosity of the soil. This is difficult in usual circumstances, but it could be done in detail in microfluidic situations, where artificial media with controlled porosity may be built and where solute concentration may be measured with high precision, especially in two-dimensional arrays [22–25] much used for DNA chromatography. Since DNA is a charged molecule (a polyelectrolyte) the detailed analysis involving it would be more complicated than the one presented here, which is valid for neutral polymers.

The fact that a test of the details of our equations could be difficult in practice in situations where such details as matrix porosity and polymer concentration are not known with precision, does not mean that they have no practical interest: Indeed, they predict a dependence of the polymer extraction rate as a function of the solvent flow rate which is different from that of the conventional theory, as plotted in Figs. 4 and 5. Thus, one could check the mentioned flow-rate dependence and compare it with the one expected in usual models ignoring the dependence of the free energy of the polymer solution on the viscous pressure.

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