Comment on "Osmotic Propulsion: The Osmotic Motor"

In a recent Letter [1] it has been claimed that colloidal particles immersed in a multicomponent fluid would be subject to an "osmotic force" $\mathbf{F}^{\text{osm}} = -\int_{S_p} \Pi d\mathbf{A}$ if a solute concentration gradient exists. Here $\Pi = nk_BT$ denotes an osmotic pressure, n the solute concentration, T denotes temperature, and $d\mathbf{A}$ is an area element pointing outward of the particle surface S_p. In addition, the authors of Ref. [1] claimed that the balance of this "osmotic force" with Stokes friction $\mathbf{F}^{\text{osm}} + \mathbf{F}^{\text{hyd}} = 0$, $\mathbf{F}^{\text{hyd}} = -6\pi\eta a\mathbf{U}$ would determine the propulsion velocity $\mathbf{U}$ of a spherical particle of radius a in the fluid [1]. Colloidal particles are indeed set in motion in a concentration gradient of a solute even though there is no force acting [2–4]. The claims of Ref. [1], however, violate basic physical principles and are fundamentally flawed as we clarify here.

First, Osmotic pressures do not generate forces on colloidal particles, but only act at semipermeable membranes. Since the solvent passes this membrane [which separates two compartments (1) and (2) and which is impermeable to the solute], the chemical potentials of the solvent $\mu_s^{(1)} = \mu_s^{(2)}$ balance. In an incompressible fluid $\mu_s \simeq -k_BTnv_s + Pv_s$ for small solute concentration. Here, P denotes pressure and v_s is the solvent molecular volume. A hydrostatic pressure difference emerges, $\Delta P \simeq k_BT(n^{(2)} - n^{(1)})$. Note that the pressure difference appears only after the balance of the chemical potential of the solvent is reached. The corresponding momentum source is provided by the membrane.

The scenario proposed in Ref. [1] does not take the effects of the solvent properly into account and violates momentum conservation [3]. Momentum conservation implies a balance equation for the momentum density $\rho\mathbf{v}$, where ρ denotes mass density and $\mathbf{v}$ is the local center-of-mass velocity. This balance reads

$$\frac{\partial \rho v_\alpha}{\partial t} = \partial_\beta \sigma_{\alpha\beta} + f_\alpha^{\text{ext}}. \quad (1)$$

Here, f_α^{ext} is the external bulk force density, applied, for example, by gravitation or electromagnetic fields. The stress tensor $\sigma_{\alpha\beta}$ describes momentum fluxes and accounts for internal forces due to the interactions between atoms and molecules. In a Stokes regime or in stationary conditions, $\partial \rho v_\alpha/\partial t$ can be neglected and force balances can be expressed as

$$\partial_\beta \sigma_{\alpha\beta} + f_\alpha^{\text{ext}} = 0. \quad (2)$$

For a Newtonian fluid in the Stokes regime, the stress tensor is $\sigma_{\alpha\beta} = \sigma_{\alpha\beta}^d - P\delta_{\alpha\beta}$, where $P = -\partial F/\partial V|_{N_i}$ is hydrostatic pressure. Here, F denotes the bulk free energy of the multicomponent fluid, the derivative is taken with respect to volume V for fixed number of molecules N_i of all components i. The dissipative stress results from shear and compression and is given by

$$\sigma_{\alpha\beta}^d = \eta(\partial_\alpha v_\beta + \partial_\beta v_\alpha - \tfrac{2}{3}\partial_\gamma v_\gamma \delta_{\alpha\beta}) + \bar{\eta}\partial_\gamma v_\gamma \delta_{\alpha\beta}, \quad (3)$$

where η and $\bar{\eta}$ are the shear and bulk viscosities, respectively. In the case of an incompressible fluid with $\nabla \cdot \mathbf{v} = 0$, Eqs. (2) and (3) imply the Stokes equation

$$\eta\Delta\mathbf{v} = \nabla P - \mathbf{f}^{\text{ext}}. \quad (4)$$

Osmotic pressure does not contribute to the stress $\sigma_{\alpha\beta}$ and osmotic pressure gradients do not generate forces on immersed particles. Stokes friction describes the situation where an external body force $F_\alpha^{\text{ext}} = \int_{V_p} f_\alpha^{\text{ext}} dV = -\int_{S_p} \sigma_{\alpha\beta} dA_\beta$ is acting on a colloidal particle of volume V_p. Stokes Eq. (4) with the incompressibility constraint and appropriate boundary conditions on the particle surface [3] determine the barycentric flow and the pressure field in the fluid. This implies that the full stress profile in the fluid is obtained by solving the Stokes equation and there are no other contributions from osmotic effects. The pressure P is determined by the incompressibility condition and not by concentration gradients of solutes.

In order to highlight the mistake of Ref. [1], consider as a specific example pure water H_2O as a solvent in which heavy water D_2O is dissolved. The scenario of Ref. [1] then implies that colloidal particles move in the presence of a D_2O gradient in H_2O at a speed depending on an entropic effect, independent of molecular masses. However, solvent and solute differ only in their molecular mass and any physical effect should vanish with vanishing mass difference. This is not possible with the scenario of Ref. [1]. The reason for this failure is that this scenario ignores contributions of the solvent concentration gradient which exactly cancel the force invoked in Ref. [1].

The authors of Ref. [1] do not distinguish properly between "external forces" and "generalized thermodynamic forces." The latter are not real forces, which enter momentum balances, even though they can induce motion. In multicomponent fluids no force of osmotic origin is exerted on colloidal particles. Stokes friction applies only if external forces such as gravity move a particle in a fluid [3].

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[1] U. M. Córdova-Figueroa and J. F. Brady, Phys. Rev. Lett. **100**, 158303 (2008).
[2] J. Anderson, Annu. Rev. Fluid Mech. **21**, 61 (1989).
[3] F. Jülicher and J. Prost, Eur. Phys. J. E **29**, 27 (2009).
[4] M. N. Popescu et al., J. Chem. Phys. **130**, 194702 (2009).