

## Comment on “Osmotic Propulsion: The Osmotic Motor”

In a recent Letter Córdova-Figueroa and Brady [1] claim to explain the autonomous motion of colloidal particles that catalyze a chemical reaction at one side of the colloid. They claim to explain a motion of the colloid not arising due to inertial thrust by ejecting exhaust, but due to forces on the colloid generated from a self-generated solute gradient. Such an explanation violates Newton’s law of action equals reaction as well as the first law of thermodynamics. The bottleneck of the reaction at the colloid is the diffusive transport of reactants and products to and from the catalytic site on the colloidal particle. The reaction is assumed to be isothermal with vanishing internal energy of reaction  $\Delta U_r = 0$ . Such motion of the colloidal particle cannot be chemically propelled motion. The only change in thermodynamic potential is due to the entirely entropic mixing of reactants and products. Our claim is that the free energy of mixing cannot be used to propel the catalytic sphere. This can be seen if we shut off the chemical reaction and only rename each molecule of type “*b*” into “*c*” once it comes into contact with the catalytic site. A renaming cannot propel the catalytic sphere. The sphere is surrounded by the same type of molecules in an equilibrium configuration and the number of renamed molecules is increasing while the number of molecules keeping their old names is decreasing. There will be a concentration gradient of each subset of molecules creating an osmotic force onto the catalytic sphere, the sum of which obviously needs to vanish. Both subsets of molecules diffuse but in a way such that no total osmotic pressure arises. The interdiffusion of molecules happens in mechanical equilibrium. If we artificially distinguish between molecules of type *b* and molecules of type *c*, then there is an increase of free energy due to the increase in entropy of mixing as molecules of type *c* are created. No heat,  $Q = 0$ , is associated with this change since it is completely irreversible. The internal energy of the system does not change,  $\Delta U = 0$  and the first law of thermodynamics predicts  $W = \Delta U - Q = 0$ . No work can be done by the mixing of artificially renamed molecules. The argument does not change in a real athermal chemical reaction with products having different transport properties than the reactants. Irreversible changes of the entropy cannot be converted into work. The creation of an osmotic pressure gradient  $\nabla p$  requires the power density  $P = \nabla \cdot (\mathbf{v}p)$  which is not supplied by the chemical reaction from which we deduce that  $\mathbf{v} = \mathbf{0}$ . It is a violation of Newton’s law that diffusion should create a pressure gradient. Since every force of a particle *b* onto the sphere *a* will cause a counter force in the opposite direction of the sphere *a* onto the particle *b* (Newton’s law of action equals reaction) the particle *b* and the sphere *a* will both move to reduce an osmotic gradient. The Stokes drag velocities  $v_a/v_b = -b/a$  are such that small molecules react faster than large particles. Any osmotic pressure

gradient will be decomposed by the solvent, reactants and products faster than via the motion of the large sphere “*a*”. It is unclear how an osmotic pressure gradient (usually arising due to a diffusive equilibration of the solvent in the presence of a *quenched* solute) should be produced faster than its mechanical decomposition. Mechanical equilibration times are faster than a diffusive equilibration of the system. A motor if supplied locally with fuel will move with a speed determined by the efficiency to convert its power into motion irrespective of any conditions far away. It is irrelevant for the motor whether the system is open or closed. Even if the decrease in free energy of mixing would drive the motion it would not describe a chemically propelled motor but an externally driven sphere since the free energy consumption rate depends on the concentration  $n_b^\infty$  far away from the motor. The motor cannot overcome the threshold toward autonomous motion because its performance is locked to an insufficient external supply rate upholding a steady state condition. A functioning chemically propelled motor requires more than chemical nonequilibrium. Experiments [2–5] on the autonomous propulsion of catalytic nanoparticles are performed exclusively with exothermic chemical reactions with only a minute fraction of the chemical power converted into propulsive motion. Theoretical descriptions of the autonomous motion [1,6,7] should include a fuel performing an exothermic reaction at the catalytic site that supplies the chemical energy for the propulsion.

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