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Role of Interfacial Entropy in the Particle-Size Dependence of Thermophoretic Mobility

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We show that changes in the surface tension of a particle due to the presence of nonionic surfactants and impurities, which alter the interfacial entropy, have an impact on the value of the thermophoretic mobility. We have found the existence of different behaviors of this quantity in terms of particle size which can be summarized through a power law. For particles that are small enough, the thermophoretic mobility is a constant, whereas for larger particles it is linear in the particle radius. These results show the important role of the interfacial entropic effects on the behavior of the thermophoretic mobility.

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Particles movement induced by temperature gradients [1] known as the Soret effect has been the subject of many experimental and theoretical studies in recent years [2–5] due to its importance in areas as diverse as soft condensed matter, biophysics, microgravity, and nanoscience. Thermophoresis may, for example, be used for the control of colloids and macromolecules [6] and to implement effective particle separation methods [7] and focusing techniques [8]. Studies on thermophoresis have also shown their importance in the deposition of micro- and nanoparticles [9] in laminar [10] and turbulent [11] pipe flows, removing and collecting aerosol particles [12] and in biotechnological applications [13,14].

Crucial to the study of the motion of the particles is the knowledge of the thermophoretic mobility $\mathcal{D}_T$, the proportionality factor between the thermophoretic velocity $\vec{v}_T$ and the temperature gradient ∇T: $\vec{v}_T = -\mathcal{D}_T \nabla T$, and whether it depends on the particle size or not. There is no general consensus on this question [15]. Experiments performed with polystyrene solid particles of sizes between 40 nm and 2 μm in Tris buffer solution, show a linear dependence of the thermophoretic mobility on the particle radius a [16] whereas others made with n-alkane liquid particles in water or surfactant ranging from 5 to 16 nm support the fact that the mobility does not depend on the particle radius [17,18]. An experiment carried out with latex particles in a solution containing tetrabutylammonium perchlorate with particle radius ranging from 100 to 400 nm [19], supported by simulation results of rigid particles with radius in the interval 36 to 154 nm [20] shows a decreasing behavior of the thermophoretic mobility as a function of the particle radius. These different behaviors of $\mathcal{D}_T$ may be due to the fact that more than just a single driving force determines the thermophoretic force in experimental systems, each with a different size dependence. The thermophoretic force may result from the temperature response of the core material of the particles relative to that of the solvent, the possible presence of electrical double layers, and from the distribution of surfactant and fluid molecules at the interface which affects the interfacial entropy. To analyze the origin and the role of the interfacial entropic effects in thermophoresis is the main objective of this Letter.

The thermophoretic velocity can be obtained from hydrodynamics by computing the force exerted by the solvent on a particle moving with a given velocity in the presence of a temperature gradient [21–24]. The force contains a thermophoretic contribution proportional to the temperature gradient [25]. A general expression valid when the particle is a drop, a bubble, or a solid particle with a monolayer of adsorbed solvent [26–28] was given in Ref. [23]: $\vec{F} = -\mu^{-1}\vec{u} + \mathcal{D}_T \mu^{-1} \nabla T$, where μ is the mobility. Under the hydrodynamic approach, $\mathcal{D}_T$ is proportional to the derivative of the surface tension with respect to the temperature $\gamma_T \equiv d\gamma/dT$ and to the particle radius (a) and is a function of the viscosities and thermal conductivities of the inner and outer fluids.

In our analysis, we show how the distribution of the nonionic solvent and surfactant molecules adsorbed at the interface may depend on the size of the particle. Since this distribution affects the interfacial entropy, it may bring about a dependence of the surface tension and, consequently, of the γ_T factor on particle size. We thus find that for sufficiently large particles, the ratio between the numbers of fluid and surfactant molecules on the particle surface does not depend on the radius (a). Therefore, γ_T does not depend on a and so the thermophoretic mobility is a linear function of a. On the contrary, for small particles that ratio may depend on the radius of the particle due to entropic effects which lead to a different behavior of γ_T as a function of a.

To show how the distribution of fluid and surfactant molecules at the interface affects the thermophoretic velocity, we will consider the stationary movement of a drop immersed in a fluid subjected to a temperature gradient. Both the fluid inside the drop and the surrounding fluid are assumed to be multicomponent, incompressible, and Newtonian. Quantities inside and outside the drop and at the interface will be denoted by the subindexes i, o, and s, respectively.

To compute γ_T, we use the Gibbs-Duhem relations for the inner (i) and outer (o) fluids and the interface (s) to obtain

$$-A d\gamma = S^{(s)} dT + N_1^{(s)} d\mu_1^{(s)} + N_2^{(s)} d\mu_2^{(s)}, \tag{1}$$

$$-V^{(\beta)} dp^{(\beta)} = S^{(\beta)} dT + N_1^{(\beta)} d\mu_1^{(\beta)} + N_2^{(\beta)} d\mu_2^{(\beta)}. \tag{2}$$

The fluids in each subsystem have two components indicated by subindexes 1 and 2. In Eq. (2), $\beta = i,\ o$. Moreover, A is the surface area of the particle, N the number of molecules, μ the chemical potential, V the volume, and S the entropy.

We consider equipotential systems for which $d\mu_1^{(\beta)} = -d\mu_2^{(\beta)}$ and rewrite the number of molecules of the j component as $N_j^{(\beta)} = N^{(\beta)} x_j^{(\beta)}$, with $x_j^{(\beta)}$ the molar fraction in the subsystem β. Moreover, we assume that the radius of the particle is constant and use $d(p^{(i)} - p^{(o)}) = 2d(\gamma/a)$ obtained from the Young-Laplace equation for a constant particle radius. These assumptions together with equilibrium conditions ($d\mu_j^{(i)} = d\mu_j^{(s)} = d\mu_j^{(o)}$), leads to

$$\gamma_T = -\rho_a \frac{[s^{(s)} - \delta x^{(s)} (\frac{\Delta(\rho s)}{\Delta[\delta(\rho x)]})]}{1 + \frac{2}{a} \frac{\delta x^{(s)}}{\Delta[\delta(\rho x)]} \rho_a}. \tag{3}$$

Here $\rho_a \equiv N/A$ is the interfacial density, $s^{(s)}$ the interfacial entropy per mol, $\delta y^{(\beta)} \equiv y_1^{(\beta)} - y_2^{(\beta)}$ in which y could be a thermodynamic variable (x, s, ρ among others), $\Delta(\rho s) \equiv (\rho s)_i - (\rho s)_o$, with ρ the molar density, and $\Delta(\delta \rho x) \equiv [\delta(\rho x)]_i - [\delta(\rho x)]_o$. Defining $s^* \equiv s^{(s)} - \delta x^{(s)} (\Delta(\rho s)/\Delta[\delta(\rho x)])$ as the surface entropy considering the difference in the changes of the chemical potential of the components with temperature and introducing a Tolman-like length [29] $\delta = \{\delta x^{(s)}/\Delta[\delta(\rho x)]\}\rho_a$, we obtain

$$\gamma_T = -\rho_a \frac{s^*}{(1 + \frac{2\delta}{a})}. \tag{4}$$

From this expression, we conclude that when the size and number of surfactant molecules increases, the number of configurations available for the molecules of the fluid decreases and therefore the interfacial entropy decreases and so does γ_T. For a one-component system ($x^\beta = 1$) forming two phases (bubble in liquid or drop in vapor), for which $\delta x^{(s)} = 1$ and $\Delta[\delta(\rho x)] = \rho^i - \rho^o$, i.e., $\delta = \rho_a/(\rho^i - \rho^o)$, the length δ converges to Tolman's length [29].

The analysis of how surface tension depends on the radius of the particle was performed in Ref. [29] for only one component by assuming that ρ_a and the temperature are constant. In general, however, we could expect a nonuniform distribution of the solvent molecules with the particle size in the interfacial region, mainly in small enough droplets. We can thus express the interface density as

$$\rho_a = \rho_a^{(\infty)} \Omega(a), \tag{5}$$

where $\rho_a^{(\infty)} \equiv N^{(\infty)}/A$ is the surface density at a sufficiently large particle radius and $\Omega(a)$ is a function accounting for finite-size effects in the surface density that we have to determine.

Considering an ideal interface for which $s^* = s_1^* x_1^{(s)} + s_2^* x_2^{(s)}$ and large enough particles, we then obtain

$$\gamma_T^\infty = -s^* \rho_a^{(\infty)} = x_1^{(s)} \gamma_{T,1}^{(\infty)} + x_2^{(s)} \gamma_{T,2}^{(\infty)}, \tag{6}$$

in which $\gamma_{T,1}^{(\infty)}$ and $\gamma_{T,2}^{(\infty)}$ are usually reported in the literature for pure liquids and large systems [30]. Finally, the general expression for γ_T in an ideal system in which the size of the particle does not change with the temperature, is given by

$$\gamma_T = \Omega(a) \frac{\gamma_T^{(\infty)}}{(1 + 2\frac{\delta}{a})}. \tag{7}$$

When this expression is integrated in temperature, one obtains a generalization of Tolman's formula for the surface tension valid for multicomponent systems and by taking finite-size effects into account [29].

For a nonideal interface, the surface tension derivative with respect to the temperature for large systems is in this case given by

$$\hat{\gamma}_T^{(\infty)} = \gamma_T^{(\infty)} + f(x_j^{(s)}, T), \tag{8}$$

where the term f is a nonideal surface entropy that may in general depend on the interfacial molar fractions and temperature. It considers the changes in the surface entropy caused by surfactants or impurities adsorbed on the interface.

For a nonconstant particle radius and by performing an analogous procedure to the one above, we can then arrive at general expression for γ_T in which nonideal interactions are also considered:

$$\gamma_T = \frac{\Omega(a)}{(1 + 2\frac{\delta}{a})} \left(\hat{\gamma}_T^{(\infty)} + \frac{2\delta}{3a} \gamma k_v \right), \tag{9}$$

where $k_v = (1/v_o)(dv_o/dT)$ is the thermal compressibility coefficient.

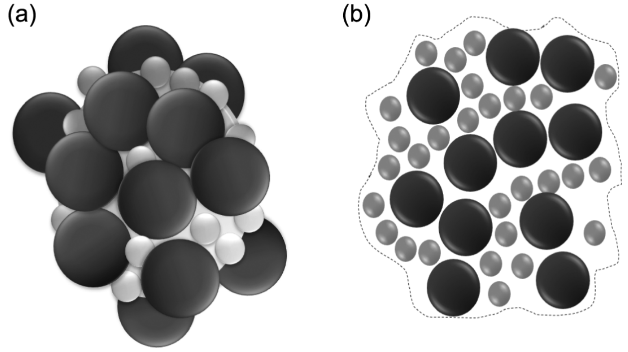

FIG. 1. (a) Fluid (gray) and surfactant (black) molecule distribution in the interface of a spherical particle of radius a. (b) Distribution of fluid and surfactant molecules in a spot of the interface.

To compute $\Omega(a)$, we first find the number N of fluid molecules at the interface whose available space is affected by the presence of impurities and surfactants (see Fig. 1). The area of the particle surface occupied by the N fluid molecules is $N\pi r_0^2/\phi$, where r_0 is the radius of a molecule and ϕ the packing factor of the interface. Values of ϕ fall in the interval $0.34 \leq \phi \leq 0.5$ [31]. For a liquid interface like ours, we chose the lowest value, $\phi \approx 0.34$. Analogously, the surface area occupied by the surfactant molecules is $N'\pi r_s^2/\phi$, where N' is their number and r_s their radius. The surface area covered by both fluid and surfactant molecules is then $M = (\pi/\phi)Nr_0^2[1 + (r_s/r_0)^2 N'/N]$, where the ratio between surfactant and fluid molecules depends on the surface molar fraction of surfactant in the interface ($x_3^{(s)}$), $N'/N = x_3^{(s)}/(1 - x_3^{(s)})$.

To obtain the number of solvent molecules on the surface, we use the constraint $M < 4\pi a^2$ in the previous expression of the area covered by fluid and surfactant molecules M. The value of N is then given by the floor function

$$N = \left\lfloor \frac{(4\phi)(a/r_0)^2}{[1 + g(a)]} \right\rfloor, \tag{10}$$

where the quantity $g(a) \equiv (r_s/r_0)^2 N'/N$ compares the areas of the particle surface covered by fluid molecules and surfactant.

In Fig. 2(a), we plot the total number of molecules on the interface ($N_t \equiv N + N'$) for the cases N'/N constant and N'/N linear in a. Both behaviors lead to a constant $\mathcal{D}_T$ and to a $\mathcal{D}_T$ linear in a. Curves intersect at a value of the particle radius a_0, below which the total number of particles is higher for the case $N'/N \sim a$ than when $N'/N \sim$ const. Contrarily, above a_0 only the opposite is true. Figure 2(b) shows that the area not covered by particles ψ is larger in the first case at values of the radius $a < 13$ nm. A linear dependence of N'/N on a and, equivalently, a linear dependence of $g(a)$ on a is thus entropically more favorable for $a \leq a_0$, where a_0 is a threshold radius at which the ratio between the number of molecules of surfactant and the fluid in the interface becomes constant. Notice that the factor $g(a)$ can be expressed as

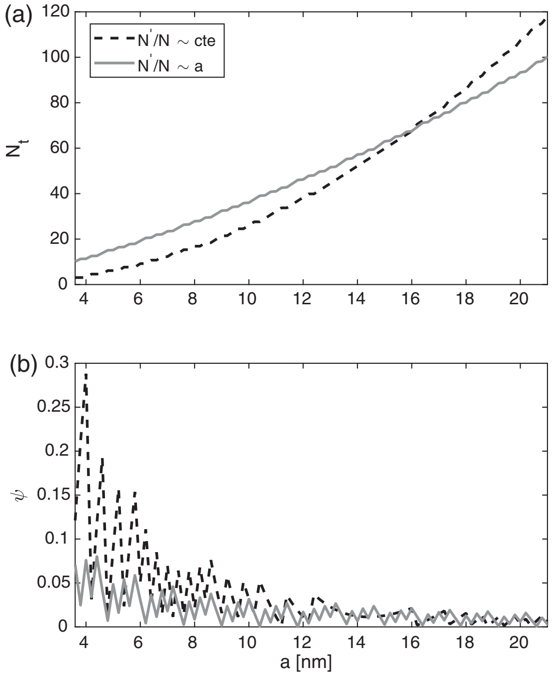

FIG. 2. (a) Total number of molecules on the surface $N_t = N + N'$ for different particle radii a[nm]. (b) fraction of the particle-free area $\psi \equiv 1 - M/4\pi a^2$. The black dashed line corresponds to a constant value of N'/N and the gray continuous line to a linear dependence of N'/N on the particle radii a. Both behaviors lead to a constant $\mathcal{D}_T$ and to a $\mathcal{D}_T$ linear in a.

$$g(a) = g(a_0)[\Theta(a - a_0) + (a/a_0)\Theta(a_0 - a)], \tag{11}$$

where

$$g(a_0) = \left(\frac{r_s}{r_0}\right)^2 \left(\frac{N'}{N}\right)_{(a_0)}. \tag{12}$$

For a monolayer composed by only fluid molecules, the number of molecules on the interface is approximately $N^{(\infty)} = \pi\phi(a/r_0)^2$. Therefore, by considering Eq. (5), for which $\Omega(a) = N/N^{(\infty)}$ and using Eq. (10), the finite-size effects in the surface density can thus be evaluated through the relation

$$\Omega(a) = \frac{1}{\pi\phi(a/r_0)^2} \left\lfloor \frac{4\phi(a/r_0)^2}{1 + g(a)} \right\rfloor. \tag{13}$$

Using the representation of the floor function in Fourier series [32], we approximate the surface density as $\Omega(a) \approx 4/\pi[1 + g(a)] - 1/N_\infty + \sum_k \sin[8N^{(\infty)}/1 + g(a)]/\pi k N^{(\infty)}$.

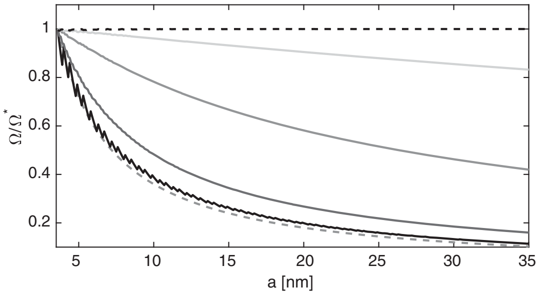

FIG. 3. Function Ω/Ω^* versus particle radius a where Ω^* denotes the maximum value of Ω. Continuous black, dark gray, gray, and light gray lines correspond to $r_s/r_0 = 12$, 6, 3, 1.5, respectively, whereas the dashed black line is the result for $x_3^{(s)} = 0$. As a reference, The dashed gray line decreasing as $1/a$ serves as a reference.

For $N^{(\infty)} \gg 1$, we can approximate $\Omega \approx 4/\pi[1 + g(a)]$. This behavior explicitly shows how the presence of surfactant molecules on the surface mediated by steric and excluded volume effects affects the distribution of fluid molecules and thus the surface tension.

In Fig. 3, we show the behavior of $\Omega(a)$ for a monolayer interface with $r_0 = 0.32$ nm and threshold radii $a_0 = 32$ nm for different values of the ratio r_s/r_0. To illustrate the behavior of this function, we use the approximation $x_3^{(s)} \approx \Phi(r_s/r_0)$, where Φ is the volume fraction of the surfactant in the solution, with $\Phi \approx 0.029$ [18]. From the figure, we observe the power law behavior $\Omega \sim 1/a^\alpha$ with $0 < \alpha < 1$. In particular, $\Omega \sim 1/a$ for $r_s/r_0 = 12$ and the curve exhibits sharp behavior due to the discrete nature of N inherent to the floor function of Eq. (10). By decreasing r_s/r_0, Ω tends to a constant.

To further verify the validity of our model, we will consider the case of a nonelectrolytic system of n-alkane water with a nonionic surfactant studied in Refs. [18,33] and compare the results of our model with the experimental data [18]. We will assume that the molecular radius, surfactant fraction, and behavior with the temperature is the same for each n alkane [18]. Moreover, based on the experimental result that the thermophoretic mobility is proportional to the temperature [34,35], we will assume that the function f accounting for the nonideal behavior of the interface is linear in the temperature. In order to consider the surface entropy change by adsorption of surfactant molecules, f must also be proportional to the surface area covered by the surfactant $g(a)$. To account for changes in the direction of the thermophoretic velocity reported in Ref. [18] at a certain transition temperature T_t, we write $f(T) = k_f g(a)(T - T_t)$, where k_f is a fitting parameter.

To obtain the surface tension, we integrate Eq. (9) in the temperature for $r_s = 12r_0$ and $a_0 = 16$ nm and use k_f to fit the experimental data [18,36]. The values of k_f for each n alkane fall between 2.5 to 5.4 $[\mathrm{mJ/m^2\,K^2}]$. Figure 4 shows the behavior of γ as a function of T, evidencing an accurate matching of model results and experimental data for each n alkane. The dashed black curve gives the surface tension for a constant value of N/A [29], which does not reproduce the experimental data for n octane. This feature supports our contention that N/A must be a function of particle size.

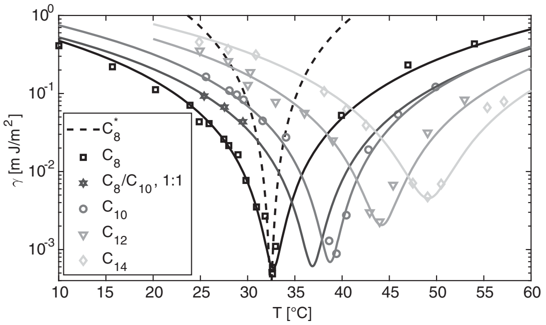

FIG. 4. Surface tension versus temperature for different hydrocarbons (n-octane C_8, equimolar mixture of n-octane/n-decane C_8/C_{10}, n-decane C_{10}, n-dodecane C_{12}, and n-butadecane C_{14}) components in a surfactant water system. The continuous lines represent model results and geometric forms show experimental data. C_8^* corresponds to the case N/A constant.

The thermophoretic mobility can be obtained from hydrodynamics [23] and is proportional to γ_T in the form

$$\mathcal{D}_T = -\frac{2a\gamma_T}{\eta_0}\frac{1}{(2 + \lambda_i/\lambda_o)(2 + 3\eta_i/\eta_o)}, \qquad (14)$$

where $\eta_{i,o}$ and $\lambda_{i,o}$ are the viscosities and thermal conductivities of the inner i and outer o fluids. Our analysis of γ_T then leads us to know how the thermophoretic mobility behaves in accordance with the size of the particle. This expression does not consider the thermodynamic properties of the core material that may have an impact on the total mobility, as happens in the case of Janus particles that exhibit an internal mass gradient [37,38].

In Fig. 5(a), we show the behavior of γ_T as a function of the particle size for the family of the n alkanes studied in Ref. [18], evaluated at $T = 27$ °C. Since the n-alkanes have similar physicochemical properties, we plot γ_T for the family of n alkanes, inferring the behavior: $\gamma_T \propto 1/a$. In the figure, we also compare the results obtained from our model with experiments [18]. The thermophoretic mobility as a function of the particle size is shown in Fig. 5(b). We observe that it varies smoothly around the constant value 3.54 $\mu\mathrm{m^2/Ks}$, as commented in Refs. [17,18]. These variations could be a consequence of the small size of the particles [39] in whose case a continuous variation of their surface area is not necessarily followed by a constant change of their covered area, as illustrated in Fig. 2(b).

In this range of particle sizes, one can question the validity of a purely thermodynamic treatment due to a greater importance of fluctuations at those scales [40] and to the possible existence of a strong coupling between

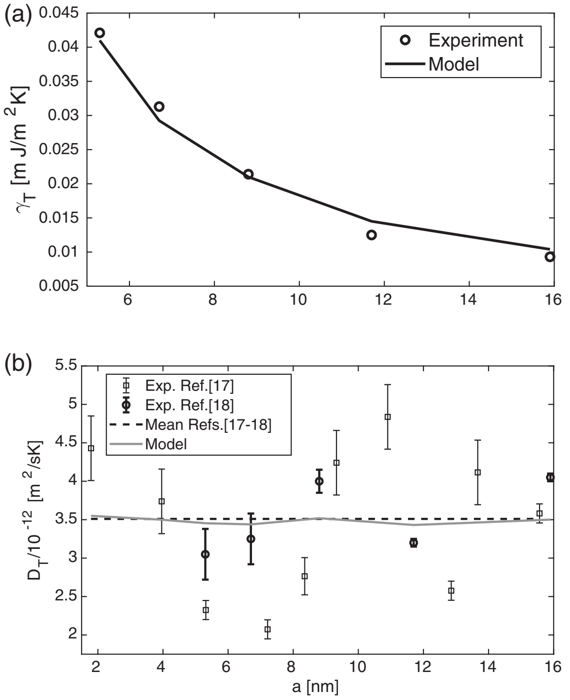

FIG. 5. (a) γ_T factor versus particle radii a[nm]. Here $\gamma_T \propto 1/a$. (b) Thermophoretic mobility $\mathcal{D}_T$ versus particle radius for $T = 27\,°\mathrm{C}$. The continuous line corresponds to model results and the symbols to experimental data from Refs. [17,18].

particle and bath that may modify the thermal response of the particle [41]. To estimate the impact of these factors on the thermophoresis phenomenon is currently an unsolved problem.

By using Eq. (14) and considering the behavior of Ω shown in Fig. 3 and Eq. (9), we infer the power law for the thermophoretic mobility $\mathcal{D}_T \propto a^{1-\alpha}$ in which the exponent α depends on how the surfactant molecules are distributed on the particle surface. The value $\alpha = 0$ corresponds to a size-independent distribution which results in a linear behavior of $\mathcal{D}_T$ with the particle radius, similar to the one observed in Ref. [16] for charged particles. Interfacial entropic effects could in this case contribute to the thermal response of the particle. It has been indicated that this linear behavior is not reproduced by means of a pure hydrodynamic treatment for charged particles [42]. When $\alpha = 1$ the fraction of the covered area by the surfactant on the interface increases linearly with the radius and consequently $\mathcal{D}_T$ does not depend on the size of the particle, as observed experimentally in Refs. [17,18]. In the case in which $\alpha > 1$, $\mathcal{D}_T$ decreases with the particle radius, as observed in the experiments presented in Refs. [19,20]. Finally, for long enough polymers it has been observed that $\mathcal{D}_T$ does not depend on their length [43]. This result can be explained from our theory if we model the unrolled polymer as a set of bonded spheres having the same radius. Since the radius is small we conclude that the effective $\mathcal{D}_T$ is a constant.

In summary, we have shown that the presence of fluid and surfactant molecules adsorbed on the particle surface modifies the interfacial entropy and in turn the surface tension. This feature has an impact on the thermophoretic mobility which in general fulfills a power law in the particle radius. We have found the tendency that for particles that are small enough, the thermophoretic mobility is a constant whereas for larger particles it is linear in the radius. Our results show how and under what conditions interfacial entropic effects play a relevant role in the behavior of thermophoretic mobility.

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