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### I. Introduction

Light has become a standard and versatile tool to control the motion of colloidal particles. The position and velocity of colloidal particles can be manipulated by directly transferring photonic momentum to the particles, as in the case of optical tweezers<sup>1</sup> and light-driven microscale rotors.<sup>2,3</sup> Moreover, light has a significant heating effect when absorption by the colloidal particles or the solvent is strong. Thus, light is often used to heat the solution to disturb the system.<sup>4,5</sup> In particular, when heating is nonuniform, thermal gradients can drive a directional transport of the colloidal particles by thermophoresis.<sup>6–9</sup> This has been widely exploited in the manipulation of colloidal particles and the design of colloidal devices.<sup>10–19</sup>

When the heated region is close to a boundary, thermal gradients can cause a long-ranged thermoosmotic flow along the boundary wall,<sup>6,20–23</sup> which may have an influence on the colloidal structure and dynamics. The thermoosmosis generated by the walls could thus introduce an extra parameter to control the motion of the colloidal particles. However, to date the thermoosmotic effects have been hardly investigated. By contrast,

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# Dynamics of a colloidal particle near a thermoosmotic wall under illumination<sup>†</sup>

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The effects of light on colloidal particles in solution are multiple, including transfer of photonic linear/ angular momentum and heating of the particles or their surroundings. The temperature increase around colloidal particles due to light heating can drive a thermoosmotic flow along a nearby boundary wall, which significantly influences the motion of the particles. Here we perform mesoscopic dynamics simulations to study two typical scenarios, where thermoosmosis is critical. In the first scenario, we consider a light-absorbing colloidal particle heated by uniform illumination. Depending on the fluid–wall interactions, the thermoosmotic flow generated by the wall can exert a long-ranged hydrodynamic attraction or repulsion on the "hot" Brownian particle, which leads to a strong accumulation/depletion of the particle to/from the boundary. In the second scenario, we investigate the motion of a colloidal particle confined by an optical tweezer in a light-absorbing solution. In this case, thermoosmosis can induce a unidirectional rotation of the trapped particle, whose direction is determined by thermoosmotic properties of the wall. We show that colloidal particles near a thermoosmotic wall exhibit rich dynamics. Our results can be applied for the manipulation of colloidal particles in microfluidics.

> the wall-induced diffusio- and electroosmotic effects on the colloidal dynamics due to chemical inhomogeneities have been widely observed and exploited in recent experiments of active colloids. The relevant examples include the colloidal surfers (swimmers) on the substrate driven by nonsymmetric diffusioosmosis,<sup>24,25</sup> the steering of chemically active particles at the diffusioosmotic surfaces,<sup>26,27</sup> and the osmotic flowinduced hydrodynamic interactions.<sup>28,29</sup> Although the underlying mechanisms are quite different, thermoosmotic and diffusioosmotic phenomena share many similarities. It is therefore natural to expect that the wall-generated thermoosmosis is able to play an important role in nonisothermal colloidal suspensions, particularly in microfluidic and highly confined environments.

> In the paper, by means of computer simulation we study the dynamic behaviors of a single colloidal particle close to a thermoosmotic wall in the presence of a light-induced temperature gradient. We consider two representative systems. One is a light-absorbing colloidal particle moving under uniform illumination, in which the particle acts as a heat source and creates a thermal gradient.<sup>13,30,31</sup> The temperature gradient around the particle drives a thermosomotic flow along the wall, which can point toward or away from the particle depending on the thermosomotic properties of the boundary wall. The flow gives rise to a purely hydrodynamic attraction or repulsion between the hot particle and the wall, which translates into the accumulation or depletion of the particle near the wall. The other is a colloidal sphere optically trapped in a light-absorbing

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solvent,<sup>5,32,33</sup> where the thermal gradient is generated by nonuniform heating of the solvent due to highly focused illumination. In this case, the thermoosmotic flow exerts a non-vanishing torque on the trapped particle and hence results in a unidirectional rotation of the particle. These findings are in significant contrast to those obtained only with common stick or slip boundary walls. This implies that the thermoosmotic wall effects have to be properly accounted for in light-heated colloidal suspensions.

The rest of the paper is organized as follows. Section II outlines the simulation model and method. Simulation results and discussion are presented in Section III, and Section IV summarizes our findings.

#### II. Simulation method and systems

#### A. Method

Solvent. In order to bridge the large gap in time and length scales between the colloidal and solvent particles, we employ a hybrid simulation scheme. The solvent is modeled by a particlebased mesoscale approach known as multiparticle collision dynamics (MPC),<sup>34-37</sup> while the colloid particle is described using the standard molecular dynamics (MD) method. In the MPC approach, the fluid is represented by N point particles, with mass m, position  $r_i$ , and velocity  $v_i$  of particle i. The particle dynamics consists of alternating streaming and collision steps. In the streaming step, the solvent particles move ballistically for a time step  $\Delta t$ ,  $r_i(t + \Delta t) = r_i(t) + v_i(t)\Delta t$ . In the collision step, particles are sorted into a cubic lattice with cells of size  $l_c$ , and their velocities relative to the center-of-mass velocity of each cell are rotated by an angle around a randomly oriented axis,  $v_i(t + \Delta t) = v_{\rm cm}(t) + \Re(v_i(t) - v_{\rm cm}(t))$ . Here,  $v_{\rm cm}$  is the center-ofmass velocity of the collision cell, and the rotational matrix  $\Re$  is determined by requiring local angular momentum conservation in one single direction (say the z direction).<sup>18</sup> This is relevant for studying the dynamics of an optically trapped particle, which is expected to rotate unidirectionally due to the wall-generated thermoosmosis. To guarantee Galilean invariance, the grid of collision cells is randomly shifted before each collision step.<sup>38</sup> In the coarse-grained collision, mass, momentum and energy are locally conserved, which ensures that the method correctly captures hydrodynamic interactions, mass transport and heat conduction. Moreover, in the approach thermal fluctuations are naturally involved.

**Colloidal particle.** The colloidal particle is modeled by a single bead that interacts with the solvent *via* a Lennard-Jones (LJ)-type potential,

$$U(r) = 4\varepsilon \left[ \left(\frac{\sigma}{r}\right)^{2n} - \left(\frac{\sigma}{r}\right)^n \right] + C, \quad r \le r_c$$
(1)

with the potential intensity  $\varepsilon$ , the colloidal particle radius  $\sigma$ , and the positive integer *n* controlling the potential stiffness. Here, *C* = 0 and  $\varepsilon$  correspond to respectively the traditional and repulsive LJ-type potentials with the corresponding cutoff radius *r*<sub>c</sub>. Moreover, in order to model the rotational diffusion of the colloidal particle a sticky boundary condition is implemented on the particle surface through a revised bounce-back collision rule,<sup>39</sup> with the collision radius  $r_{\rm bb} \simeq \sigma$ .

Boundary wall. The systems are confined by two walls in the y direction. The interactions between the colloidal particle and the wall are described by the repulsive LJ potential with n = 28and the interacting length  $\sigma_w = 1.13\sigma$ . In the simulations, we consider three types of boundary walls: stick, slip and thremoosmotic walls. The stick and slip boundaries can be trivially realized by separately performing the bounce-back operation and the specular reflection of the velocity of the solvent particle upon collision with the wall.<sup>35,37</sup> The thermoosmotic wall can be similarly implemented at the mesoscale level by adding a driving operation to the stick/slip boundary condition.<sup>29</sup> Briefly, by a prescribed threshold temperature  $T_{t}$ , the solvent particles within the interaction range of the wall are classified into the cold and hot particles based on their instantaneous kinetic energies. The thermoosmotic force is generated by selectively reversing the tangential velocity of one type of solvent particle. When the driving operation is performed for the hot particles, the resulting thermoosmotic flow is along the thermal gradient, corresponding to a thermophobic wall; otherwise the flow is against the thermal gradient, corresponding to a thermophilic wall. The driving operation is performed after each MPC step, such that it is independent of the MPC collision.

The magnitude of the thermoosmotic flow can be tuned by changing the threshold  $T_t$ . For fixed temperature gradients,  $T_t$ determines the thermoosmotic force. In the present systems, the thermoosmotic flow has a maximum at medium  $T_t$ , since a very large or small  $T_t$  produces a very weak thermoosmotic force. In the simulations  $T_t$  is chosen to produce a moderate flow that facilitates the measurements of thermosmotic effects while maintaining the low Reynolds number condition.

Note that in our simulations the boundary walls are always adiabatic rather than isothermal. An isothermal wall can be implemented using a boundary thermostat and does not qualitatively change the simulation results. In the simulation we do not use the ghost particle technique for the wall.<sup>46</sup> This is because the velocities of the ghost particles need to be drawn from the Maxwellian distribution with a prescribed temperature, which corresponds to an isothermal wall.

Simulations are performed with the average number density of fluid particles  $\rho = 10$  and the MPC time step  $\Delta t = 0.1$ . For the MD part, the equation of motion is integrated using the velocity Verlet algorithm with time step  $\delta t = \Delta t/50$ . All the quantities are expressed in terms of the MPC units by setting a = 1, m = 1 and  $\varepsilon = 1$ . With these parameters, the Schmidt number is around 3.0 and the dynamics of the MPC solvent is liquid-like.<sup>18,39</sup>

## B. System I: light-absorbing colloidal particles under uniform illumination

The simulation box is a cuboid of dimensions  $L_x \times L_y \times L_z = 40 \times 30 \times 40$ , with periodic boundary conditions in the *x* and *z* directions and the wall boundary in the *y* direction. The colloidal sphere of radius  $\sigma = 3$ , which is heated by homogeneous light radiation, moves freely in the solution, as sketched in Fig. 1(a).



**Fig. 1** (a) Schematic diagram of the light-absorbing colloidal particle under uniform light radiation. (b) The *xy* cross-section of the steady-sate temperature distribution around the colloidal particle, with the heated temperature  $T_{\rm h} = 1.0$  and the mean system temperature  $\bar{T} = 0.5$ . The grey sphere refers to the hot colloidal particle.

The particle–solvent interaction is chosen to be a repulsive LJ potential of n = 24, which produces a very small thermal diffusion factor  $\alpha_T \simeq 11$  obtained by additional simulations.

In our simulation, the illuminating light is not explicitly modelled. The light-heating effect on the colloidal particle is realized by utilizing a boundary thermostat on the particle surface to heat the surrounding solvent. Specifically, the thermal kinetic energy of the fluid particles within a thin layer around the colloidal sphere is rescaled to a high temperature. In the heating layer the energy is not locally conserved, so that the heat conduction in this layer is not properly captured. The heating approach also neglects heat transfer from the colloidal particle to the fluid, since the colloidal particle lacks internal degree of freedom. However, outside the thin layer, the energy is locally conserved such that the heat conduction process is physically correct. Consequently, the resulting temperature field is compatible with the heat diffusion equation, which has been verified in the previous work.<sup>16</sup> The input energy is drained from the system by thermalizing the mean temperature of the solution,  $\bar{T}$ , to a lower fixed value. For a small flow field, this is equivalent to fixing the total kinetic energy of the solution. To achieve this, each particle velocity is rescaled by the same factor at every MPC step, which is determined according to the imposed and actual mean temperature. The rescaling factor is quite close to unit, such that this operation only disturbs the system slightly. Moreover, since the factor is uniform, the temperature and fluid flow profiles are not affected. This simple thermostat maintains a steady-state temperature distribution around the colloidal particle, as the case of the hot gold Brownian particle studied in experiment.<sup>30</sup>

### C. System II: optically trapped colloidal particles in a light-absorbing solvent

In the second system, the colloidal particle of radius  $\sigma = 3$  is trapped using an optical tweezer, as sketched in Fig. 2(a). In this case the fluid instead of the colloidal particle absorbs light and creates a high temperature region around the laser focus. In experiment this can be easily realized by containing a light-absorbing dye<sup>5</sup> or matching the laser wavelength to an absorption peak of the solvent.<sup>32,33</sup> Here, the colloidal particle interacts with the solvent *via* a common LJ-type potential of n = 16 and C = 0. This attractive potential can induce a large thermophoretic force against the thermal gradient on the colloidal particle with  $\alpha_T \simeq 250$ , which pushes the colloidal particle away from the optical center.



**Fig. 2** (a) Schematic diagram of the colloidal sphere trapped optically in a light-absorbing solution. The red line refers to the laser and the arrows to the thermoosmotic flow generated by the substrate. (b) The temperature distribution produced by the light-absorbing solvent under laser radiation, with the heated temperature  $T_{\rm h} = 1.5$  and the average temperature  $\bar{T} = 1.0$ . For simplicity, the heated region is taken as a small cylinder.

The optical trap is modelled by a simple harmonic potential,  $U_{\rm op} = \frac{1}{2} \sum_{i} k_i (r_i - r_{\rm oi})^2$ , with  $i \in (x, y, z)$  and  $r_{\rm o}$  being the trap center. By this potential, the colloidal sphere is constrained in the proximity of the bottom wall with a distance to the wall,  $h = 1.5\sigma$ . The employed harmonic potential is anisotropic and its restoring constants in the y and z directions,  $k_y = k_z = 5000$ , are much larger than that of the x direction,  $k_x = 0.3$ , so the particle can move relatively freely in the x direction. This allows us to conveniently characterize the rotational dynamics of the colloidal particle. Otherwise, the particle will move isotropically in the xz plane, which although does not affects the particle's rotational behavior. The fluid is heated up in the laser focus region (the red cylindrical region of Fig. 2(b)) using a local thermostat. At the same time, the mean temperature of the solution is fixed. The system dimensions are  $L_x = 80$  and  $L_y = L_z = 40$ , with the periodic boundary conditions in the z directions and the boundary walls in the x and y directions.

#### III. Results and discussion

# A. Light-absorbing colloidal particle under uniform illumination

Under homogeneous radiation, the light-absorbing colloidal particle heats the surrounding fluid and creates a high-temperature region. Fig. 1(b) displays a typical steady-state temperature distribution around the particle close to the wall. The temperature decays with the distance to the particle. In the narrow gap between the particle and the wall the fluid temperature is relatively higher, since the adiabatic wall impedes heat conduction. This can result in a small temperature gradient in the direction perpendicular to the wall. At the *xz* plane near the wall, the fluid temperature has a significant radially symmetric gradient with respect to the projection of the particle center. As the particle approaches the wall, the tangential thermal gradient at the wall surface,  $T_{\parallel}$ , increases. It can drive a thermoosmotic flow along the wall,  $v = b\nabla T_{\parallel}$ , with the prefactor depending on the properties of both the wall and the fluid.<sup>20–22</sup>

In Fig. 3 we plot two representative fluid flow fields generated by the thremoosmotic walls due to the thermal gradient produced by the nearby hot colloidal particle. When the wall is thermophilic, the themoosmotic flow near the wall points away from the heat source (the colloidal particle) (Fig. 3(a)), as mentioned in Section II.



**Fig. 3** The *xy* cross-section of the flow fields generated by the thermoosmotic walls in the temperature gradient produced by the nearby hot colloidal particle. Here the red line is the streamline, the gray circles represent the colloidal spheres, and the color bar shows the flow speed. (a) The thermophilic wall, with the threshold temperature to implement the thermoosmotic boundary being 0.3. The inset refers to the density distribution of fluid particles. (b) The thermophobic wall, with the threshold temperature being 1.0. In both cases, the heating temperature  $T_h = 1.0$  and the mean temperature  $\bar{T} = 0.5$  are employed.

Due to the continuity condition, this flow is compensated by the downward fluid flow from the bulk solution, forming vortex structures. The downward compensating flow pulls the colloidal sphere toward the wall, and hence results in a purely hydrodynamic attraction between the particle and the wall. The flow patterns are reversed for a thermophobic wall. The thermoosmosis along the thermal gradient leads to a fluid flow into the bulk in the proximity of the heat source, as shown in Fig. 3(b). As a consequence, the hot colloidal particle is pushed away from the wall, resulting in a repulsive particle-wall hydrodynamic interaction.

It is known that the MPC fluid obeys the ideal gas equation of state and is compressible, as can be seen from the fluid density distribution (the inset of Fig. 3). However, the compressibility hardly influences the flow field (hence the thermoosmotic wall effect), since the Mach number is very low (<0.01). This has been confirmed in the previous works,<sup>39,42</sup> in which the temperature gradient-induced flow fields obtained by the MPC simulation quantitatively agree with the theoretical calculation with incompressible condition.

Because of the hydrodynamic attraction or repulsion, the hot colloidal particle shows a strong accumulation or depletion at the wall. Fig. 4 shows the probability density to find the particle at a distance from the wall. The results clearly show that for the thermophilic wall the hot particle is accumulated at the surface of the wall; while depleted for the thermophobic wall.



**Fig. 4** Probability distribution of the freely moving colloidal particle as a function of the distance to the wall, with different heating temperatures,  $T_{\rm h}$ . Here, y = 15 corresponds to the middle of the system. (a) The thermophilic wall, where the threshold temperature is set as 0.3. (b) The thermophobic wall with the threshold temperature 1.0. In both cases, the system mean temperature is fixed  $\bar{T} = 0.5$ . The symbols of  $T_{\rm h} = 0.5$  (red star) thus refer to the probability distribution of the non-light-absorbing particle.

The magnitude of the accumulation or depletion increases monotonically with the intensity of the thermoosmotic flow, hence with the heating temperature for fixed  $\bar{T}$ . For comparison, we also plot the probability density of a non-light-absorbing particle, which is uniformly distributed in space except at the wall due to the excluded volume interactions. The accumulation or repulsion is further quantified by defining the surface excess of the particle,  $\Gamma = 1 - \rho_{\rm b}(L_{\rm y} - 2\sigma_{\rm w})$  with  $\rho_{\rm b}$  being the bulk probability density of the colloidal particle. In the calculation  $\rho_{\rm b}$ is chosen as the one at  $y = L_y/2$ . Indeed, the surface excess plotted in Fig. 5 monotonically increases and decreases with  $T_{\rm h}$  at the thermophilic and thermophobic walls, respectively. We point out that the colloidal thermophoresis due to the existence of the local high-temperature region between the particle and the wall (see Fig. 1(b)) does not contribute to the particle accumulation or depletion, since the particle employed in the simulation only has a very small  $\alpha_{T}$ .<sup>9</sup> This is confirmed by the uniform probability distribution of the hot particle moving near a slip wall, as shown in the inset of Fig. 5.

The small thermal diffusion factor, which is achieved using the repulsive LJ potential of high exponent (n = 24), allows us to study the thermoosmotic-wall effect exclusively. When considering a particle with large  $\alpha_{\rm T}$  or low *n*, the colloidal thermophoresis perpendicular to the wall cannot be ignored. This will cause an extra accumulation or depletion of particle, depending on the sign of  $\alpha_{\rm T}$ . On the other hand, the wall-generated thermoosmotic flow is independent of  $\alpha_{\rm T}$  or the exponent *n*. Our conclusion that the thermoosmotic wall can lead to a purely hydrodynamic attraction



**Fig. 5** Surface excess of the colloidal particle as a function of the heating temperature. For comparison the inset plots the particle probability distributions for the thermophilic, thermophobic and slip boundary walls, with the same  $T_{\rm h} = 1.0$ .

or repulsion between the particle and the wall holds for general colloids. For large  $\alpha_{\rm T}$ , the total particle accumulation or depletion includes both the thermossmotic and thermophoretic contributions.

To summarize this section, the thermoosmotic wall-induced hydrodynamic attraction or repulsion has a large effect on the hot colloidal particles near the boundary. This effect cannot be captured by the stick or slip boundary. When the hot particle is far away from the wall, it only experiences a free Brownian motion and the thermoosmotic effect is negligible, since the tangential thermal gradient at the wall surface is vanishingly small. As the particle approaches the wall, the tangential thermal gradient and the generated thermoosmotic flow increase. The thermoosmotic effect is particularly relevant in microfluidic channels, where the size of the colloids is often comparable to channel diameters. More interestingly, the hot colloidal particle will always suspend in the middle of the microchannel comprised of thermophobic walls. Although here we consider a uniformly heating colloidal particle, similar behaviors can also be expected for Janus particles.

# B. Optically trapped colloidal particles in a light-absorbing solvent

Different from the first system, here the colloidal particle is optically trapped in the vicinity of the wall, and the fluid instead of the particle absorbs the light. Thus, the fluid at the center of the laser focus has the highest temperature, as shown in Fig. 2. Because the laser trap is close to the wall, there exists a large tangential component of the thermal gradient at the wall surface, distributing radially symmetrically with respect to the trap center. For the thermoosmotic wall, the tangential gradient drives a thermoosmotic flow parallel to it, which affects the motion of the trapped particle. In the present system the colloidal particle interacts with the fluid *via* a soft attractive LJ potential, so that the particle deviates from the trap center. As discussed in Section II, the trapped potential is anisotropic with a small restoring coefficient in the *x* direction. The particle

thus has two stable equilibrium points symmetrically locating on the left and right sides of the laser focus. Otherwise, if the trap is isotropic the stable positions on the *xz* plane will form a circle around the trap center. At the equilibrium point, the optical force on the particle is balanced by the thermophoretic force and the one exerted by the thermoosmotic flow.

In the present situation, besides the thermoosmotic flow generated by the boundary wall, the reaction of the thermophoretic force on the particle can also drive a fluid flow around the particle along the thermal gradient. The superposition of the two flows constitutes the total flow field, as plotted in Fig. 6. Since the wall-generated thremoosmotic flow decays with the separation from the wall, it can not only exert a force but also a torque on the trapped particle. The direction of the torque is directly determined by the thermoosmosis at the wall surface. If the colloidal particle stays at the stable point on the left side of the optical center, it will spin clockwise around the *z* axis for the thermophilic wall, and anticlockwise for the thermophobic wall. The rotation reverses when the particle locates at the right equilibrium point.

In Fig. 7 we plot the position distribution and the corresponding spin velocity,  $\Omega$ , of the trapped particle near various boundary walls. Here, we only consider the case of the particle at the left stable point. The trapped particle indeed experiences a unidirectional rotation (Fig. 7(a) and (b)). The rotational directions are opposite for the thermophilic and thermophobic walls, consistent with the above discussion. The rotational speed enhances as the separation between the particle and the optical center decreases. This is because the thermal gradient, hence the thermore, the thermosomosis along the thermophobic wall points toward the heat source, such that the stable point of the particle near the thermophobic wall is closer to the trap center than that in the case of the thermophilic wall.

As discussed in Section II.C, the attractive LJ potential of n = 16 is here employed to obtain a moderate deviation of the particle from the trap center. The symmetry breaking is necessary to observe the unidirectional rotation of the colloidal particle. Modifying the exponent *n* changes the thermoporetic force on the particle (*e.g.* the use of higher *n* reduces  $\alpha_T^9$ ), and



**Fig. 6** The cross-section of the flow fields generated by the thermophobic colloidal particle optically trapped in the light-absorbing solvent close to the thermophobic wall. The center of the optical trap is in the red area, and the gray circle refers to the colloidal sphere. Here, the vortex is formed due to the back flow induced by the side and the top walls.



**Fig. 7** The *x*-axis position distribution (blue star, the left longitudinal axis) and the corresponding rotational velocity (red triangle, the right longitudinal axis) of the optically trapped particle close to different types of boundary walls. The rotational velocity is given only in the region, where the particle probability density is prominent. Here, the positive direction of the rotation is counter-clockwise, and the coordinate of the optical trap is x = 40. (a–d) Are the thermophilic, thermophobic, slip and stick boundary walls, respectively. For the stick wall in (d), the red triangles refer to the rotational velocity in the case of the purely bounce-back operation, and the black squares to the rotational velocity in the case of the modified operation.

hence the extent of the particle deviation, but leaves the thermoosmotic flow unchanged. Thus, different colloid-solvent potentials only have a quantitative effect on the present results as long as the symmetry breaking occurs.

Fig. 7(c) indicates that even the colloidal sphere trapped near the slip wall has a non-vanishing spin velocity. Here, the unidirectional rotation arises from the wall-induced deformation of the thermophoretic flow field, which is fundamentally different from the mechanism in the case of thermosomotic walls. For a colloidal particle fixed at  $r_p = (x_p,h,z_p)$  in a nonisothermal bulk solution, the flow field at  $r = (r_x,r_y,r_z)$  due to the reaction of the thermophoretic force reads

$$v_i(r) = \frac{f_{\mathrm{T}j}}{8\pi\eta} \left\{ -\left(\frac{\delta_{ij}}{\tilde{r}} + \frac{\tilde{r}_i \tilde{r}_j}{\tilde{r}^3}\right) + \sigma^2 \left(\frac{3\tilde{r}_i \tilde{r}_j}{\tilde{r}^5} - \frac{\delta_{ij}}{\tilde{r}^3}\right) \right\}$$
(2)

with the indexes *i* and  $j \in (x,y,z)$ ,  $\eta$  being the solvent shear viscosity and  $f_{Tj}$  the thermophoretic force on the particle.<sup>40–42</sup> Here,  $\tilde{\mathbf{r}}$  denotes the position relative to the particle center  $\tilde{\mathbf{r}} = \mathbf{r} - \mathbf{r}_p$  and  $\tilde{r} = |\tilde{\mathbf{r}}|$ , and the Einstein summation convention is employed. Using the reflection method, the distortion of the flow field by the wall can be determined by considering an image particle with respect to the wall.<sup>43,44</sup>

When the wall is slip the flow field due to the image particle is simply

$$v_i'(\mathbf{r}) = \frac{f_{\mathrm{T}j}}{8\pi\eta} \left\{ -\left(\frac{\delta_{ij}}{\tilde{r}'} + \frac{\tilde{r}_i'\tilde{r}_j'}{\tilde{r}'^3}\right) + \sigma^2 \left(\frac{3\tilde{r}_i'\tilde{r}_j'}{\tilde{r}'^5} - \frac{\delta_{ij}}{\tilde{r}'^3}\right) \right\}$$
(3)

with  $\tilde{\mathbf{r}}' = \mathbf{r} - \mathbf{r}_{p}'$  being the position relative to the image particle at  $r_{p}' = (x_{p}, -h, z_{p})$ . Here, we only take into account the nearest wall in the *y* direction. The total flow is the superposition of the flow fields in eqn (2) and (3). In terms of Faxén's theorem,<sup>45</sup> the rotation of the particle is determined by the curl of the flow field generated by the image particle,  $\Omega \simeq \frac{1}{2} \nabla \times \mathbf{v}'(\mathbf{r}_p)$ , where the curl is taken at  $\mathbf{r}_p$ . Considering the fact that the thermophoretic force is parallel to the *x* axis and against the thermal gradient, we have  $\nabla \times v'(\mathbf{r}_p) = -f_T/(16\pi\eta h^2) > 0$ . This explains the counter-clockwise rotation of the colloidal particle locating at the left-side stable point. By substitution of the thermophoretic force measured in the simulation,  $f_T \simeq -4.5$ , into the above expression, we have  $\Omega \simeq 0.4 \times 10^{-3}$ . The obtained spin velocity compares well to the simulation results in Fig. 7(c).

On the other hand, for a stick wall the flow field due to the image particle reads  $^{43,44}$ 

$$\begin{aligned} v_{i}^{\,\prime}(\mathbf{r}) &= \frac{f_{\mathrm{T}j}}{8\pi\eta} \bigg\{ \left( \frac{\delta_{ij}}{\tilde{r}'} + \frac{\tilde{r}_{i}^{\,\prime}\tilde{r}_{j}^{\,\prime}}{\tilde{r}'^{3}} \right) - 2h \big( \delta_{j\alpha}\delta_{\alpha k} - \delta_{jy}\delta_{yk} \big) \\ &\times \frac{\partial}{\partial \tilde{r}_{k}^{\,\prime}} \bigg[ \frac{h\tilde{r}_{i}^{\,\prime}}{\tilde{r}'^{3}} - \left( \frac{\delta_{iy}}{\tilde{r}'} + \frac{\tilde{r}_{i}^{\,\prime}\tilde{r}_{y}^{\,\prime}}{\tilde{r}'^{3}} \right) \bigg] \bigg\}, \end{aligned}$$
(4)

with  $\alpha \in (x,z)$ . Note that eqn (4) only includes the Stokeslet part of the flow field due to the image particle, and higher-order terms are neglected. Taking the curl of the flow field at  $r_{\rm p}$  yields  $\nabla \times \mathbf{v}'(\mathbf{r}_{\rm p}) = f_{\rm T}/(16\pi\eta h^2) < 0$ , implying a clockwise spin. This contradicts with the one measured in the simulation (Fig. 7(d)), in which the particle experiences a very small anticlockwise rotation. The discrepancy may originate from the following facts. First, the bounce-back collision rule used in the simulation cannot realize a strict nonslip wall,46 giving rise to a partially slip boundary. Second, the bounce-back rule can induce a small thermoosmotic flow toward the heat source due to the thermal creep effect,<sup>47,48</sup> which is a rarefied gas effect and cannot be completely avoided in the coarse-grained fluid.<sup>42</sup> Third, the above calculation ignores the contributions coming from other walls at  $y = L_y$ , x = 0 and  $x = L_x$ , in principle which can be included by multiple reflections. Finally, the higher-order terms due to the image particle (such as source dipole) are not accounted for. Clearly, the first two factors are responsible for the slightly positive rotation.

In order to support the argument, we perform an additional simulation with a more stick wall than the purely bounce-back one. This is achieved by combining the bounce-back rule with the driving operation applied for both the hot and cold solvent particles (*i.e.* all the solvent particles within the boundary layer). Such a modified operation can indeed lead to a more stick boundary.<sup>29</sup> Moreover, the driving operation implemented for both types of particles does not cause extra thermoosmosis. The obtained rotational velocity of the colloidal particle is plotted in Fig. 7(d) (the black squares), which indicates that the particle rotates at a low rate clockwise instead of anticlockwise. This is well consistent with the above argument. For the modified stick wall, we cannot avoid weak thermoosmoosis induced by the bounce-back operation due to the thermal creep,<sup>42</sup> such that it still results in a difference in the magnitude of the rotational velocity between the theoretical prediction and the simulation.

Before closing this section, we would like to comment on the use of isothermal or thermally conductive walls. In the present simulations the walls are always adiabatic, as mentioned in Section II.A. When considering isothermal or conductive walls, the temperature distribution may be affected in two ways. First, the temperature difference between the heating area and the wall can introduce a temperature gradient perpendicular to the wall. This will lead to an extra particle accumulation/depletion by the colloidal thermophoresis. Second, the fluid temperature gradient parallel to the wall will be weakened, such that the thermoosmotic flow decreases (but the flow direction remains unchanged). This reduces the magnitude of the thermoosmotic-induced particle accumulation/depletion or rotation. All these do not result in qualitatively different results. Thus, the conclusions obtained with the adiabatic wall also hold for isothermal or thermally conductive walls.

### IV. Conclusion

In the paper, we performed computer simulations to study the effect of the thermoosmosis generated by the boundary wall on the motion of colloidal particles under radiation. We separately simulated a light-absorbing colloidal particle under uniform illumination and an optically trapped particle in a light-absorbing solvent. In both situations the heating effect from the light could drive a thermoosmotic flow along the nearby boundary wall. For the lightabsorbing particle, the thermoosmotic flows generated by the thermophilic and thermophobic walls exert a purely hydrodynamic attraction and repulsion on the "hot" particle, respectively. This translates into a strong particle accumulation or depletion near the wall surface. For the light-absorbing solvent, the thermoosmotic flow applies a hydrodynamic torque on the optically trapped particle, such that it spins unidirectionally with its rotational direction determined by the wall thermoosmotic properties. Our results indicate that the colloidal particle in the vicinity of the thermoosmotic wall demonstrates rich dynamic behaviors, which cannot be captured by only considering the common slip or stick wall. It is therefore necessary to properly account for the wall-induced thermoosmosis in non-isothermal solutions. Our findings can be easily verified in colloidal experiments.

The results in the paper are not limited to optical heating; other heating methods, such as exothermal reaction or contact heating, can similarly drive thermoosmosis. Thus, the wall-induced thermoosmosis is expected to play a role in a wide range of systems. The thermoosmotic effect would be of particular importance in microand nanofluidic environments and in the performance of microscale devices that often operate close to the boundary wall.

### Conflicts of interest

There are no conflicts to declare.

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