

## Anisotropic Memory Effects in Confined Colloidal Diffusion

Sylvia Jeney,<sup>1,\*</sup> Branimir Lukić,<sup>1</sup> Jonas A. Kraus,<sup>2,1</sup> Thomas Franosch,<sup>2</sup> and László Forró<sup>1</sup>

<sup>1</sup>*Institut de Physique de la Matière Complexe, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland*

<sup>2</sup>*Arnold Sommerfeld Center for Theoretical Physics (ASC) and Center for NanoScience (CeNS), Department of Physics, Ludwig-Maximilians-Universität München, Theresienstraße 37, D-80333 München, Germany*

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The motion of an optically trapped sphere constrained by the vicinity of a wall is investigated at times where hydrodynamic memory is significant. First, we quantify, in bulk, the influence of confinement arising from the trapping potential on the sphere's velocity autocorrelation function  $C(t)$ . Next, we study the splitting of  $C(t)$  into  $C_{\parallel}(t)$  and  $C_{\perp}(t)$ , when the sphere is approached towards a surface. Thereby, we monitor the crossover from a slow  $t^{-3/2}$  long-time tail, away from the wall, to a faster  $t^{-5/2}$  decay, due to the subtle interplay between hydrodynamic backflow and wall effects. Finally, we discuss the resulting asymmetric time-dependent diffusion coefficients.

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Understanding and controlling the transport of colloidal microcarriers, such as membrane vesicles, through a fluid is one of the main challenges in cell biology [1] and related lab-on-a-chip approaches. With the miniaturization of such technologies, particularly microfluidics [2], the colloid's motion is increasingly confined, and the influence of boundaries, e.g., a channel wall, becomes non-negligible. In particular, in a system as small as a cell, many obstacles will alter the trajectory of a diffusing particle. Any deviation from its well-understood free Brownian motion will give information on the particle's surroundings. The reduction of a colloid's mobility close to a wall, also known as "surface confinement," was already predicted by Lorentz in 1907 [3,4], and is expected to entail drastic effects on its time-dependent Brownian motion arising from the thermal fluctuations in the system.

Experimental evidence for this wall effect is comparably recent and consists mostly in measuring changes in the diffusion coefficient  $D$  of a micron-sized sphere approaching a surface [5,6] or being confined between two walls [7–9]. Measurements confirm that an interface increases the steady-state friction; hence, the viscous drag on the particle, slowing down its diffusion as the distance  $h$  between the sphere's center and the surface, is reduced. The motion becomes anisotropic in the directions parallel and perpendicular to the wall. Conventional data acquisition and analysis rely on Lorentz's zero-frequency approximation for the mobility, which only takes a viscous contribution from the fluid into account. However, for a neutrally buoyant sphere, the presence of hydrodynamic memory due to momentum conservation in the fluid [10–12] leads to it having a significantly delayed dynamic behavior, at time scales much larger than the particle's momentum relaxation time  $\tau_p = 2a^2\rho_p/9\eta$ . This memory has been observed in bulk for colloidal suspensions [13,14], and, more recently, directly for a single microsphere [15,16]. Its origin lies in the backflow that a spherical particle of density  $\rho_p$  and radius  $a$  creates in a fluid of viscosity  $\eta$  and

density  $\rho_f$ . The long-time diffusion of momentum in the viscous fluid leads to an algebraic decay, the so-called long-time tail, in the velocity autocorrelation function (VACF)  $C(t) = \langle v(t)v(0) \rangle \simeq D\sqrt{\tau_f/4\pi t}^{-3/2}$  of the fluctuating sphere at times  $t \gtrsim \tau_f = \rho_f a^2/\eta$ , the time needed by the perturbed fluid flow field to diffuse over the distance of one particle radius. Obviously, the presence of a wall bounding the fluid will affect the fluid vortex once it has encountered the wall, which will occur at times larger than its propagation time,  $\tau_w = h^2\rho_f/\eta$ , from the particle to the boundary [17]. Computer simulations for a colloidal particle in confinement [18,19] confirm that the wall has drastic effects on the long-time behavior and induces different exponents for the algebraic decay depending on geometry.

In this Letter, we investigate the effect of hydrodynamic vortex diffusion on the nature of the long-time tail as a function of the wall-particle distance  $h$ , by measuring the position fluctuations of a single spherical particle approaching a hard surface. Weak optical trapping [20] is employed to position a silica sphere relative to a plain glass surface, and, at the same time, to track the Brownian particle's trajectory interferometrically [21] with a precision better than 1 nm and a time resolution of 2  $\mu$ s [15]. The thermal position fluctuations of the sphere in the weak trap are measured with an InGaAs quadrant photodiode, amplified and digitized (12 bits). The position signal is recorded during  $t_s = 20$  s with a sampling rate  $f_s = 500$  kHz corresponding to  $N = 10^7$  data points. The Brownian particle used here is a silica sphere of several micrometers diameter ( $\rho_p = 1.96$  g/cm<sup>3</sup>) immersed in water ( $\rho_f = 1$  g/cm<sup>3</sup>,  $\eta = 10^{-3}$  Pa·s). It is gradually approached towards the surface of a 100  $\mu$ m-sized sphere sandwiched between the two coverslips of a fluid chamber (size  $\approx 2$  cm  $\times$  0.5 cm and thickness  $\approx 100$   $\mu$ m). As illustrated in Fig. 1, the big sphere can be considered as a flat surface on the scale of our Brownian sphere. Such a

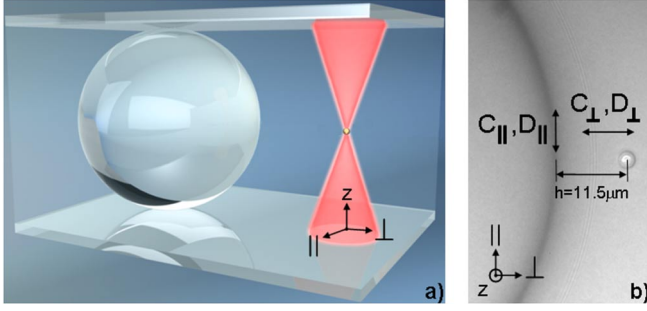


FIG. 1 (color online). (color) (a) 3D lateral view of the experiment; spheres are drawn to scale. A silica particle of radius  $a = 1.5 \mu\text{m}$  trapped by the laser focus is placed next to the surface of a significantly larger silica sphere. This  $100 \mu\text{m}$  sphere is immobilized between the two coverglass surfaces of the sample chamber. (b) Optical image of the probing particle's position relative to the wall created by the big sphere. The  $3 \mu\text{m}$  probing particle was placed at a distance  $h = 11.5 \mu\text{m}$  away from the  $100 \mu\text{m}$  sphere's surface and gradually approached. The velocity correlation functions, as well as the diffusion coefficients for the motion parallel and perpendicular to the wall, are measured.

configuration circumvents the drawback of the lower resolution along the optical axis  $z$ , intrinsic to optical trapping interferometry [22], thereby allowing measurements with comparable accuracy in both directions, parallel and perpendicular to the boundary. The sample is mounted onto a piezo-stage, and the  $100 \mu\text{m}$  sphere can be positioned at a distance  $h$  relative to the trapped particle by moving the piezo-stage in all three dimensions with a precision of  $\approx 1 \text{ nm}$ .

As a first test of the sensitivity of our setup, we measure the VACF for a microsphere ( $a = 2.25 \mu\text{m}$ ,  $\tau_p = 2.2 \mu\text{s}$ ,  $\tau_f = 5.1 \mu\text{s}$ ) far away from any boundaries ( $h \geq 40 \mu\text{m}$ ). The optical trap is particularly well-suited for the experiment, as its harmonic potential results in a linear force  $F = -kx(t)$ , which only acts on the particle, but does not confine the surrounding fluid. The spring constant  $k$  of the trap gives rise to a new time scale  $\tau_k = 6\pi\eta a/k$ . A model for the Brownian motion of a particle in a harmonic potential is provided by Clercx and Schramm [23], who went beyond a simple Stokes approximation by using the time-dependant linearized Navier-Stokes equation to describe the fluid motion. Figure 2 shows the measured normalized velocity autocorrelation function  $C(t)/C(0)$  for  $k = 19 \mu\text{N/m}$  and  $k = 5 \mu\text{N/m}$ . In order to compare data with the theoretical curves, the normalization  $C(0)$  and  $k$  are treated as fit parameters. As can be seen in Fig. 2, our data follow the theoretical prediction [23] over the full time range, down to a noise level of  $5 \times 10^{-5}$ . As was shown earlier [24], an intermediate time window  $\tau_f \lesssim t \lesssim \tau_k/20$  opens, where the particle's motion can still be observed, but is free from the influence of the trap and mainly dominated by the fluid's inertia. Hence, in order to minimize influences from the trapping potential on the

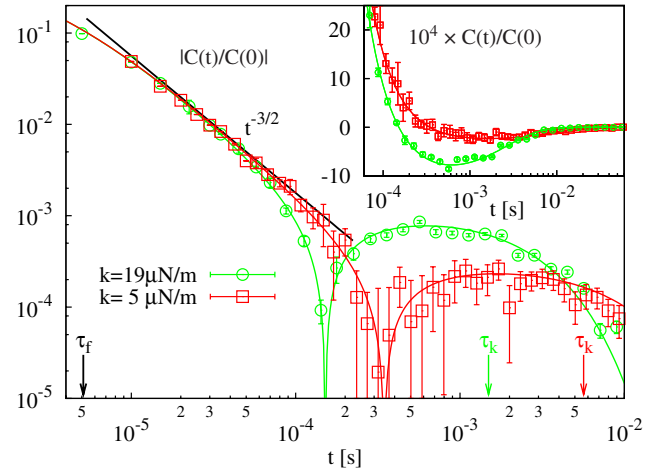


FIG. 2 (color online). (color) Log-log plot for the measured normalized velocity autocorrelation of a sphere ( $a = 2.25 \mu\text{m}$ ) held by an optical trapping potential with  $k = 19 \mu\text{N/m}$  (green circles) and with  $k = 5 \mu\text{N/m}$  (red squares). The continuous red and green lines are fits to the model of Clercx and Schramm [23]. The hydrodynamic long-time tail  $C(t) \propto t^{-3/2}$  (black line) emerges as the spring constant is decreased. Inset: Blowup of the region of anticorrelations on a log-linear scale.

Brownian motion and resolve hydrodynamic memory effects, we adjust  $\tau_k$  to be as long as possible. By decreasing the spring constant from  $k = 19 \mu\text{N/m}$  to  $k = 5 \mu\text{N/m}$ , we directly observe the emergence of the long-time anomaly  $t^{-3/2}$  (Fig. 2) over two decades in signal. In an incompressible liquid, the initial value of the VACF is determined by  $C(0) = \langle v(0)v(0) \rangle = k_B T / [\frac{4\pi}{3} a^3 (\rho_p + \frac{1}{2} \rho_f)]$  [25], leading to

$$\frac{C(t)}{C(0)} \simeq B \left( \frac{t}{\tau_f} \right)^{-3/2}, \quad t \gtrsim \tau_f, \quad (1)$$

where the amplitude  $B = (\rho_p/\rho_f + 1/2)/9\sqrt{\pi}$  depends only on the mass ratio. The value of the prefactor is of the order  $B \sim 1/10$  for the colloidal system used here, and can be directly read off the data at  $t = \tau_f$  (Fig. 2). At longer times,  $t \gg \tau_k$  ( $t = 22 \text{ ms}$  for  $k = 19 \mu\text{N/m}$  and  $t = 96 \text{ ms}$  for  $k = 5 \mu\text{N/m}$ ), the fluid's inertia is expected to generate a second zero in  $C(t)$  followed by a fast  $t^{-7/2}$ -tail as  $(15B/4)(t/\tau_f)^{-3/2}(t/\tau_k)^{-2}$ , which, however, remains unobservable due to noise.

Next, we approach the Brownian sphere ( $a = 1.5 \mu\text{m}$ ,  $\tau_p = 1 \mu\text{s}$ ,  $\tau_f = 2.25 \mu\text{s}$ ) towards the boundary created by the  $100 \mu\text{m}$  glass sphere (Fig. 1), and vary  $h$  from  $37.8 \mu\text{m}$  to  $4.8 \mu\text{m}$ , corresponding to a reduction in  $\tau_w$  from  $1400 \mu\text{s}$  to  $23 \mu\text{s}$ . The trap stiffness is minimized to  $k \approx 2 \mu\text{N/m}$  ( $\tau_k = 14 \text{ ms}$ ) by lowering the incoming laser power. It is worth noting that decreasing  $k$  degrades the signal-to-noise level, as can be seen in the increase of the error bars in Fig. 2. As already mentioned above, momentum from the fluid is transferred to the wall at times  $t \gtrsim \tau_w$ .

The leading hydrodynamic tail  $t^{-3/2}$  in  $C(t)$  is then canceled, and  $C(t)$  splits into  $C_{\parallel}(t)$  for the motion parallel and  $C_{\perp}(t)$  for the motion perpendicular to the wall. Recently, Felderhof [17] provided a full analytical solution for the motion in both directions. He generalized the frequency-dependent admittance (i.e., the frequency-dependent mobility) for the unconstrained motion  $\mathcal{Y}_0(\omega)$  [12] to  $\mathcal{Y}_{\parallel}(\omega)$  and  $\mathcal{Y}_{\perp}(\omega)$  for a point particle moving close to a wall. Relying on the fluctuation-dissipation theorem [25], he then calculated  $C_{\parallel}(t)$  and  $C_{\perp}(t)$  via a Fourier-back-transform from  $\mathcal{Y}_{\parallel}(\omega)$  and  $\mathcal{Y}_{\perp}(\omega)$ . For the parallel motion, a more rapid but still algebraic decay is predicted,

$$\frac{C_{\parallel}(t)}{C_{\parallel}(0)} \simeq \frac{3B}{2} \frac{\tau_w}{\tau_f} \left(\frac{t}{\tau_f}\right)^{-5/2}, \quad (2)$$

for  $t \geq \tau_w$ , provided that the wall is not too close;  $\tau_w \gg \tau_f, \tau_p$ . For the motion perpendicular to the wall, the long-time behavior,  $t \geq \tau_w$ , is predicted, to leading order in  $a/h$ , as

$$\frac{C_{\perp}(t)}{C_{\perp}(0)} \simeq \frac{3B}{2} \left[ A_{z3} \left(\frac{t}{\tau_f}\right)^{-5/2} + \frac{\tau_w^2}{4\tau_f^2} \left(\frac{t}{\tau_f}\right)^{-7/2} \right], \quad (3)$$

where  $A_{z3} = (2\rho_p/\rho_f - 5)/9$ .

To disentangle surface confinement from the trap constraint, we extend Felderhof's theoretical approach [17], by including the optical trapping force [26]. In bulk, the harmonic potential modifies  $\mathcal{Y}_0(\omega)$  [12] to  $\mathcal{Y}_k(\omega) = [\mathcal{Y}_0(\omega)^{-1} - k/i\omega]^{-1}$  [23]. Accordingly, in the presence of a wall, the admittances  $\mathcal{Y}_{\parallel,\perp}(\omega)$  have to be modified to  $[\mathcal{Y}_{\parallel,\perp}(\omega)^{-1} - k/i\omega]^{-1}$ , and a suitable Fourier algorithm yields the VACFs in the entire time domain, which is fitted to our data.

Figure 3 shows the normalized  $C_{\parallel}(t)$  and  $C_{\perp}(t)$ , in the time range  $\tau_f < t < \tau_k/20 = 0.7$  ms, at four different distances from the wall. Far away from the boundary, at  $h = 37.8 \mu\text{m}$ , we observe the same  $t^{-3/2}$  power-law for both directions [Fig. 3(a)]. However, as soon as the sphere reaches the proximity of the wall, and  $\tau_w$  falls into our window of observation,  $C(t)$  splits due to the hydrodynamic interaction with the wall [Fig. 3(b),  $h = 9.8 \mu\text{m}$ , and  $\tau_w = 96 \mu\text{s}$ ]. Our data show clearly that the anisotropy increases even more as  $h$  is further decreased [Figs. 3(c) and 3(d)]. The higher noise floor at smaller  $h$  probably results from scattering of the highly divergent trapping laser beam by the big sphere. Data sets that were acquired at  $h < 4.8 \mu\text{m}$  presented too much noise and were not considered.

In  $C_{\parallel}(t)$ , a transition from the free bulk behavior at  $h = 37.8 \mu\text{m}$ , characterized by the  $t^{-3/2}$  power-law [Fig. 3(a)], to confined motion, with a steeper  $t^{-5/2}$  power-law, arises in the data at  $t \simeq \tau_w$ . The effective amplitude in Eq. (2) is reduced by up to 30% due to the trap. The drop to negative values in  $C_{\parallel}(t)$  arises from anticorrelations imposed by the harmonic trapping potential and can only be captured by

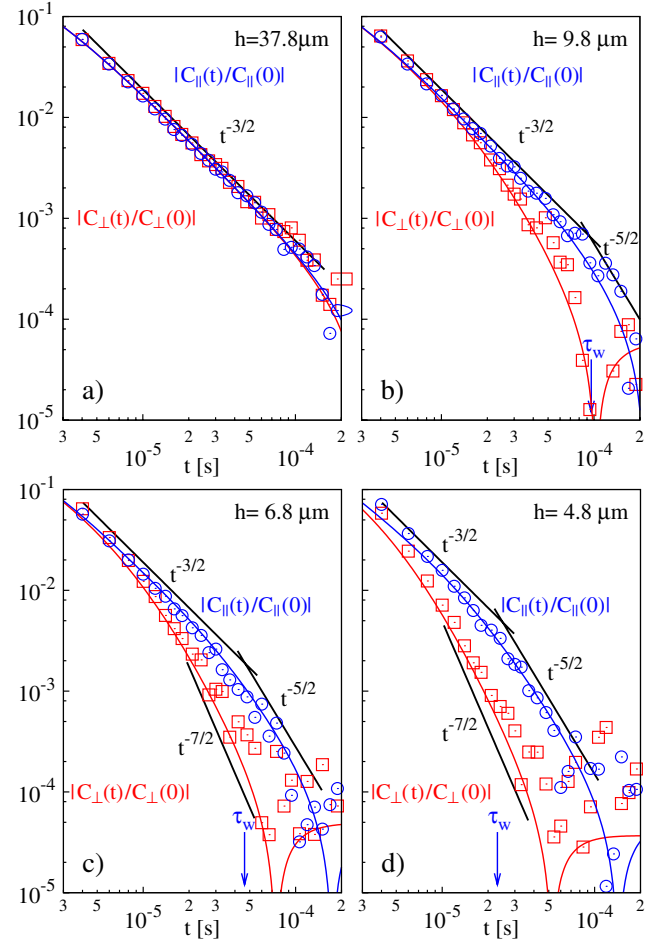


FIG. 3 (color online). Log-log plot of both normalized VACF,  $C_{\parallel}(t)/C_{\parallel}(0)$  and  $C_{\perp}(t)/C_{\perp}(0)$ , for a sphere ( $a = 1.5 \mu\text{m}$ ,  $\tau_p = 1 \mu\text{s}$ ,  $\tau_f = 2.25 \mu\text{s}$ ) trapped in a weak optical potential ( $k \approx 2 \mu\text{N/m}$ ,  $\tau_k = 14$  ms). The increasingly anisotropic VACF is measured at four distances from the wall ( $h = 37.8, 9.8, 6.8$ , and  $4.8 \mu\text{m}$ , corresponding to  $\tau_w = 1400, 96, 46, 23 \mu\text{s}$ , respectively). The characteristic power-laws from Eq. (2) and (3) are represented by black lines as guides to the eye. The experimental data (squares and circles) are compared to the theory that includes hydrodynamic memory, wall effects, and harmonic restoring forces (continuous lines).

our extended theory [26]. As can be inferred from Figs. 3, the theoretical curves describe the data down to the noise level. For the perpendicular motion, the prefactor  $A_{z3}$  of the leading  $t^{-5/2}$ -term in Eq. (3) depends on the relative densities, and is negative in our experiment,  $A_{z3} = -0.12$ . Hence, for  $k = 0$ , a sign change is expected at  $t \simeq -\tau_w^2/4\tau_f A_{z3} = 1890, 8.53, 1.96$ , and  $0.49$  ms. According to Eq. (3), a positive tail  $t^{-7/2}$  should dominate in the time window  $\tau_w \lesssim t \ll \tau_w^2/\tau_f$ . However, the sign change in  $C_{\perp}(t)$  is observed to occur much earlier, even though the trapping potential is minimal. Nevertheless, for the two closest distances [Figs. 3(c) and 3(d)], the steeper decay is compatible with the intermediate power-law  $t^{-7/2}$  pre-

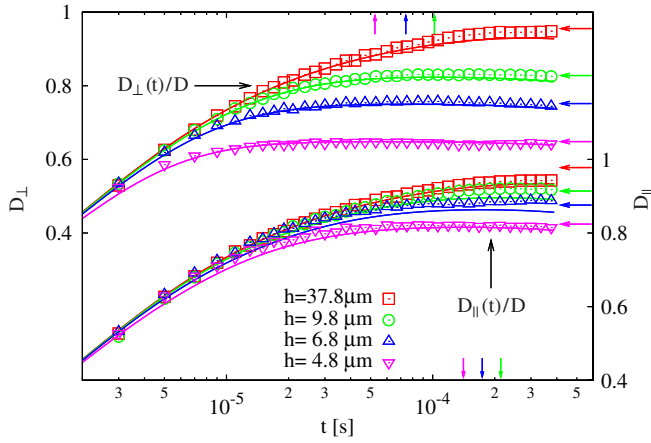


FIG. 4 (color online). Normalized time-dependent diffusion coefficients,  $D_{\parallel}(t)/D$  and  $D_{\perp}(t)/D$ , for the direction parallel and perpendicular to the wall at the same distances  $h$  as in Fig. 3. The arrows at the right correspond to the asymptotic values given by Lorentz's prediction in Eq. (4). The experimental data are represented by symbols, whereas the full lines correspond to the theoretical fits. The arrows at the top and the bottom indicate the respective time points of the shallow maxima.

dicted by Eq. (3), but with an amplitude reduced to 50% by the trap. This influence from the trap as well as noise also obscures the crossover from the positive  $t^{-7/2}$  to the negative  $t^{-5/2}$  tail.

In general, the fits in Fig. 3 are not very sensitive to the spring constant  $k$ . Therefore, we determine its value by comparing our data to the long-time behavior of the time-dependent diffusion coefficients,  $D_{\parallel,\perp}(t) = \int_0^t C_{\parallel,\perp}(t') dt'$ , shown in Fig. 4. As can be inferred from Fig. 4, the suppression of diffusion becomes anisotropic and follows the point-particle prediction by Lorentz [3],

$$D_{\parallel} = D[1 - 9a/16h], \quad D_{\perp} = D[1 - 9a/8h], \quad (4)$$

where  $D = k_B T / 6\pi\eta a$  is the diffusion constant in bulk. The higher orders in  $a/h$  are known to contribute less than 2% for  $h/a > 3$  [4], and our data analysis suggests that the point-particle limit is also valid for the time-dependent motion with similar accuracy. The observed zero crossings in the VACF translate into shallow maxima in the diffusion coefficients. They are still up to 5% below the asymptotic values  $D_{\parallel}$  and  $D_{\perp}$ , expected for  $k = 0$ , which exemplifies that free Brownian motion is not attained in optical trapping of micron-sized spheres, even for times  $t \lesssim \tau_k$ . At longer times, the trap dominates and reduces the diffusion coefficients to zero (not shown).

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\*Corresponding author: sylvia.jeney@epfl.ch

- [1] L. A. Bareford and P. W. Swaan, *Adv. Drug Delivery Rev.* **59**, 748 (2007).
- [2] T. M. Squires and S. R. Quake, *Rev. Mod. Phys.* **77**, 977 (2005).
- [3] H. A. Lorentz in *Abhandlungen über Theoretische Physik* (Teubner Verlag, Leipzig, Berlin, 1907), Vol. 1, p. 23.
- [4] J. Happel and H. Brenner, *Low Reynolds Number Hydrodynamics* (Kluwer, Dordrecht, The Netherlands, 1983).
- [5] M. D. Carbajal-Tinoco, R. Lopez-Fernandez, and J. L. Arauz-Lara, *Phys. Rev. Lett.* **99**, 138303 (2007).
- [6] E. Schaffer, S. F. Norrelykke, and J. Howard, *Langmuir* **23**, 3654 (2007).
- [7] L. P. Faucheux and A. J. Libchaber, *Phys. Rev. E* **49**, 5158 (1994).
- [8] B. Lin, J. Yu, and S. A. Rice, *Phys. Rev. E* **62**, 3909 (2000).
- [9] L. Joly, C. Ybert, and L. Bocquet, *Phys. Rev. Lett.* **96**, 046101 (2006).
- [10] V. Vladimirovsky and Ya. Terletsky, *Zh. Eksp. Teor. Fiz.* **15**, 258 (1945) [*Sov. Phys. JETP* **15**, 259 (1945)]; For an English translation, see V. Lisy and J. Tothova, arXiv:cond-mat/0410222.
- [11] B. J. Alder and T. E. Wainwright, *Phys. Rev. Lett.* **18**, 988 (1967).
- [12] E. J. Hinch, *J. Fluid Mech.* **72**, 499 (1975).
- [13] D. A. Weitz, D. J. Pine, P. N. Pusey, and R. J. A. Tough, *Phys. Rev. Lett.* **63**, 1747 (1989).
- [14] J. X. Zhu, D. J. Durian, J. Muller, D. A. Weitz, and D. J. Pine, *Phys. Rev. Lett.* **68**, 2559 (1992).
- [15] B. Lukić, S. Jeney, C. Tischer, A. J. Kulik, L. Forró, and E.-L. Florin, *Phys. Rev. Lett.* **95**, 160601 (2005).
- [16] M. Atakhorrami, G. H. Koenderink, C. F. Schmidt, and F. C. MacKintosh, *Phys. Rev. Lett.* **95**, 208302 (2005).
- [17] B. U. Felderhof, *J. Phys. Chem. B* **109**, 21406 (2005).
- [18] M. H. J. Hagen, I. Pagonabarraga, C. P. Lowe, and D. Frenkel, *Phys. Rev. Lett.* **78**, 3785 (1997); I. Pagonabarraga, M. H. J. Hagen, C. P. Lowe, and D. Frenkel, *Phys. Rev. E* **58**, 7288 (1998); I. Pagonabarraga, M. H. J. Hagen, C. P. Lowe, and D. Frenkel, *Phys. Rev. E* **59**, 4458 (1999).
- [19] D. Frydel and S. A. Rice, *Mol. Phys.* **104**, 1283 (2006).
- [20] A. Ashkin, J. M. Dziedzic, J. E. Bjorkholm, and S. Chu, *Opt. Lett.* **11**, 288 (1986).
- [21] F. Gittes and C. F. Schmidt, *Opt. Lett.* **23**, 7 (1998).
- [22] A. Pralle, M. Prummer, E.-L. Florin, E. H. K. Stelzer, and J. K. H. Hörber, *Microsc. Res. Tech.* **44**, 378 (1999).
- [23] H. J. H. Clercx and P. P. J. M. Schram, *Phys. Rev. A* **46**, 1942 (1992).
- [24] B. Lukić, S. Jeney, Z. Sviben, A. J. Kulik, E.-L. Florin, and L. Forró, *Phys. Rev. E* **76**, 011112 (2007).
- [25] R. Zwanzig and M. Bixon, *Phys. Rev. A* **2**, 2005 (1970).
- [26] J. A. Kraus, S. Jeney, B. Lukić, L. Forró, and T. Franosch (to be published); J. A. Kraus, diploma thesis, LMU München, 2007.