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## Residence and waiting times of Brownian interface fluctuations

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**Abstract** – We report on the residence times of capillary waves above a given height  $h$  and on the typical waiting time in between such fluctuations. The measurements were made on phase-separated colloid-polymer systems by laser scanning confocal microscopy. Due to the Brownian character of the process, the stochastics vary with the chosen measurement interval  $\Delta t$ . In experiments, the discrete scanning times are a practical cutoff and we are able to measure the waiting time as a function of this cutoff. The measurement interval dependence of the observed waiting and residence times turns out to be solely determined by the time-dependent height-height correlation function  $g(t)$ . We find excellent agreement with the theory presented here along with the experiments.

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**Introduction.** – The often counterintuitive field of stochastic number fluctuations has boggled the scientist's mind for ages. Svedberg's measurement of the diffusion constant [1], based on the residence times on a fluctuating number of Brownian particles in a fixed region, inspired von Smoluchowski to develop a theoretical framework for it [2,3]. His ideas were for example exploited to derive the mobility of spermatozoids [4] and white blood cells [5]. The original experiment was performed in even more detail by Brenner, Weiss and Nossal [6]. Based on Einstein's [7] and Perrin's seminal papers on Brownian motion of particles [8], von Smoluchowski [9] was the first to predict the Brownian height fluctuations of the interface. They were first theoretically treated by Mandelstam [10] and have become an important component of modern theories of interfaces [11–13]. Capillary waves were initially accessed experimentally by light [14] and X-ray scattering [15,16]. On a microscopic level capillary waves were studied in computer simulations of molecular systems [17], before recent investigations by Aarts and coworkers on colloid-polymer mixtures [18–20] added another dimension to studies on capillary waves by using confocal microscopy. In these experiments, the interfacial tension  $\gamma$  is lowered to the nN/m range. As a consequence the characteristic length and time scale of the fluctuations

are such that they can be visualized by microscopy. Microscopy furthermore enables the investigation of local phenomena such as the role of capillary waves in the rupture [21] and coalescence [22] problems. At a fixed location on the interface, the height is continuously fluctuating in time. Following Becker [23] and as sketched out in fig. 1(A) the waiting time  $\Theta$  is the average time spent in between fluctuations above a height  $h$ , and the residence time  $T$  is the average time spent above a height  $h$ :

$$\Theta(h) = \int_0^\infty dt p^-(h, t)t, \quad T(h) = \int_0^\infty dt p^+(h, t)t, \quad (1)$$

where  $p^-(h, t)$  and  $p^+(h, t)$  are the normalized distributions of time intervals of length  $t$  at a fixed position, respectively, below and above the height  $h$ . Such local measurements are not possible by scattering methods, since they require knowledge of continuous local stochastics which seem, however, easily accessible by microscopy. Pioneering work by Aarts and Lekkerkerker [24] resulted in scaling relations, but did not include a full quantitative description of the process. The crux is that however fast microscopy may be, measurements always have to be taken at discrete time intervals  $\Delta t$ , as sketched in fig. 1(B), resulting in the observed waiting and residence

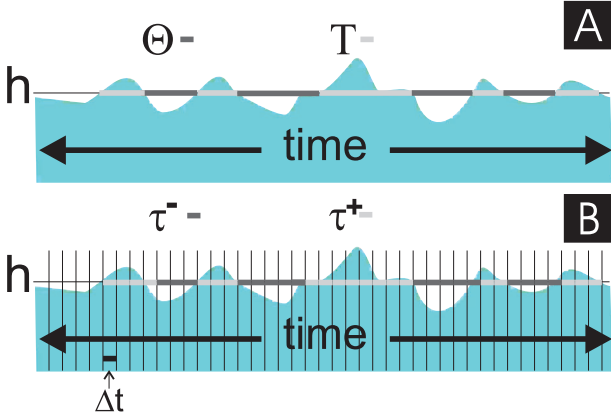


Fig. 1: (Colour on-line) (A) Variation of the interfacial height  $h$  in time with characteristic residence times  $T$  and waiting times  $\Theta$ . (B) in practice,  $T$  and  $\Theta$  are determined by discrete intervals, resulting in observed residence and waiting times  $\tau^+$  and  $\tau^-$ . These are determined by weighted averages, of the stochastics of intervals with length  $\Delta t$ .

times  $\tau^+$  and  $\tau^-$ :

$$\tau^-(h) = \sum np_n^-(h), \quad \tau^+(h) = \sum np_n^+(h). \quad (2)$$

Here,  $p_n^-$  and  $p_n^+$  are, respectively, the normalized probabilities on time intervals at a fixed position of snapshots of length  $n = t/\Delta t$ , below and above height  $h$ , with  $n$  an integer. Note that  $\tau^+$  and  $\tau^-$  are in units  $\Delta t$  and are therefore both dimensionless. Switching to discrete time intervals is not entirely trivial. Due to the Brownian character of the process, the discretisation of eq. (1) leads to statistics that depend on the chosen interval  $\Delta t$ . However, the necessity to be discrete saves rather than spoils the day, as it enables us to overcome the divergencies for continuous distributions.

**Experimental section.** – Fluorescently labeled polymethyl-metacrylate particles were prepared using the Bosma method [25], slightly modified by using decalin (Merck, for synthesis) as the reaction solvent [26]. The particle polydispersity is around 10% from scanning electron microscopy, and the dynamic light scattering particle radius is 69 nm. Polystyrene polymer ( $2 \cdot 10^3 \text{ kg mol}^{-1}$ ) with an estimated radius of gyration  $R_g$  of 42 nm [27] was added to induce depletion attraction between the colloids [28]. At sufficiently high colloid and polymer volume fractions, respectively  $\phi_c = \pi/6\sigma_c^3 n_c$  and  $\phi_p = 4/3\pi R_g^3 n_p$  (with  $n_c$  and  $n_p$  the number densities of colloids and polymers and  $\sigma_c$  the colloid diameter), this system phase separates into a colloid-rich (colloidal liquid) and a polymer-rich (colloidal gas) phase. By diluting several phase-separating samples with its solvent decalin, the phase diagram presented in fig. 2(A) was constructed. The shown binodal is a guide to the eye (the theoretical binodal appears at much lower volume fractions) and the critical point is an estimate based on the ratios of the volumes of the phases.

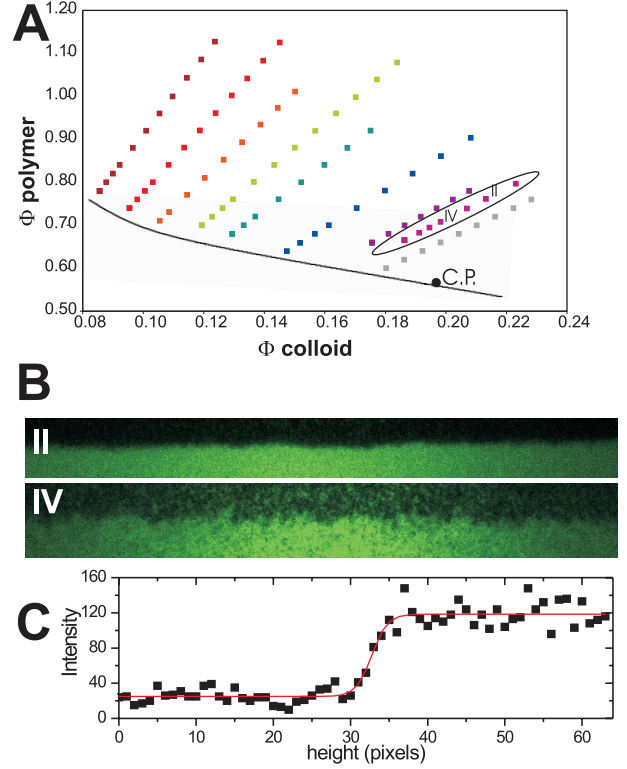


Fig. 2: (Colour on-line) (A) Phase diagram of the system studied. The dilution line studied here is marked. All shown state points phase-separate. (B) Confocal images of state points II and IV. These are pictures of a vertical cross-section of the liquid-gas interface at a given time. The horizontal axis is directed along the interface, the vertical axis perpendicular to it. (C) An example of a tanh fit for a single height of state point IV. The line is the fit, the squares are the datapoints.

A Nikon Eclipse E400 laser scanning confocal microscope equipped with a Nikon C1 scanhead was placed horizontally to study the colloid polymer mixture [26]. The microscope was furthermore equipped with a 405 nm laser and a Nikon 60 $\times$  CFI Plan Apochromat (NA 1.4) Lens. The sample container is a small glass vial, part of which is removed and replaced by a thin (0.17 mm) glass wall. Series of 10000 snapshots of the interface of  $640 \times 64$  and  $640 \times 80$  pixels were taken at constant intervals  $t_i$  of 0.45 s and 0.50 s of state points II and IV along the marked dilution line in the phase diagram, shown in fig. 2(A). The images have dimension  $100 \mu\text{m}$  along the interface *vs.*, respectively,  $10.0 \mu\text{m}$  and  $12.5 \mu\text{m}$  perpendicular to it. A single scan takes approximately 0.25 s to complete (the exact scan time does vary by a few percent in time). Typical snapshots for state points II and IV are shown in fig. 2(B). The low excitation wavelength results in resolution of  $\sim 160 \text{ nm}$ . The particles are  $\sim 138 \text{ nm}$  in diameter, hence a pixel roughly corresponds to a particle. Note that the resolution of the measured heights is significantly higher than this: the vertical location of the interface  $h(x)$  is determined for each column of pixels in a frame by fitting the pixel value  $I(z)$ , which is proportional to

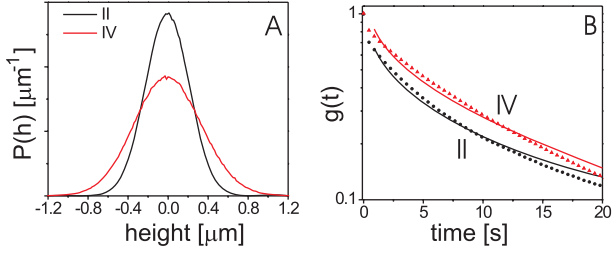


Fig. 3: (Colour on-line) Interfacial properties determined by dynamic correlation functions and height distributions for state points II and IV. (A) Height distributions for state points II and IV. (B) The dynamic correlation functions obtained for state points II and IV, normalized by  $\langle h^2 \rangle$ .

the local colloid concentration, to a van der Waals profile  $I(z) = a + b \tanh(|z - h(x)|/c)$ , as in [19]. An example for a single height is shown in fig. 2(C). The average height is set as  $h = 0$ . The exact resolution depends on the contrast between the phases, which depends on the distance to the critical point. Further away from the binodal the height fluctuations are too small, closer to the binodal the contrast between the phases reduces and the capillary waves start to show overhang effects.

**Observations and results.** – The wave heights  $h$  at an arbitrary point are distributed according to the Gaussian

$$P_{eq}(h) = \frac{\exp(-h^2/2\langle h^2 \rangle)}{[2\pi\langle h^2 \rangle]^{1/2}}. \quad (3)$$

It can be shown that  $\langle h^2 \rangle$  satisfies the expression

$$\langle h^2 \rangle = \frac{L^2}{2\pi} \int_{k_{min}}^{k_{max}} \langle |h_k|^2 \rangle k dk = \frac{k_B T}{4\pi\gamma} \ln \frac{k_{max}^2 + \xi^{-2}}{k_{min}^2 + \xi^{-2}}. \quad (4)$$

Here  $\xi = (\gamma/\Delta\rho g)^{1/2}$  is the capillary length, with  $g$  the gravitational acceleration,  $\Delta\rho$  the density difference between the two phases,  $k_B$  the Boltzmann constant,  $T$  the Kelvin temperature and  $L$  the system size. Furthermore,  $h_k$  is the amplitude of mode  $k$ ,  $k_{max} \approx 2\pi/d$  is a cutoff related to the typical interparticle distance  $d$  and  $k_{min} = 2\pi/L$  is related to the lateral system size parallel to the interface  $L$ . In eq. (4) we have used that the mean square average of  $h_k$  is given by

$$\langle |h_k|^2 \rangle = \frac{k_B T}{L^2(\Delta\rho g + \gamma k^2)}. \quad (5)$$

The height distributions are shown for state points II and IV in fig. 3(A), with  $\langle h^2 \rangle^{1/2} = 0.219$  and  $0.336 \mu\text{m}$  for state points II and IV, respectively. These will be used as a unit for the heights.

Next we consider the height correlations in time  $\langle h(t)h(t') \rangle$  at a fixed position, which we denote by  $\langle h^2 \rangle g(t - t')$ . It is calculated as [29,30]

$$\langle h^2 \rangle g(t - t') = \frac{L^2}{2\pi} \int_{k_{min}}^{k_{max}} \langle |h_k|^2 \rangle e^{-\omega_k |t - t'|} k dk. \quad (6)$$

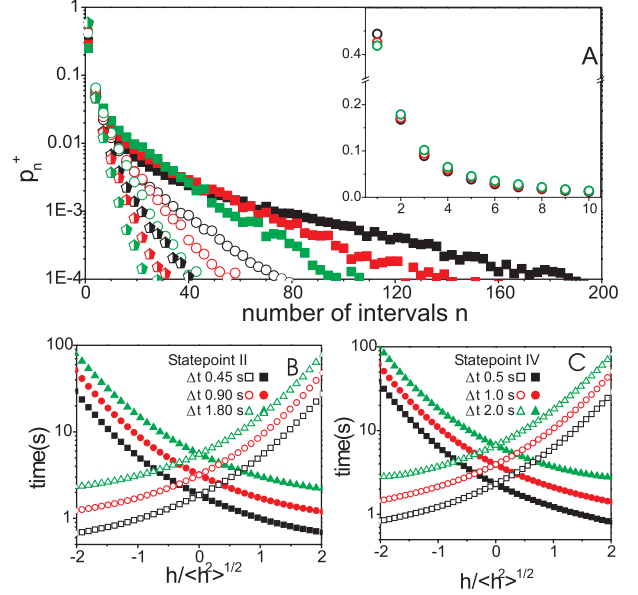


Fig. 4: (Colour on-line) (A) The distribution of observed residence times  $\tau^+$  for state point IV.  $p_n^+(h)$  is shown for  $h = -1$  (filled squares),  $0$  (circles), and  $1$  (semi-filled pentagons)  $\times \langle h^2 \rangle^{1/2}$ . The inset shows the short-time behaviour for  $h = 0$  in detail. The colours correspond to time intervals  $\Delta t = 1 t_i$  (black squares),  $2 t_i$  (red circles) and  $4 t_i$  (green triangles). (B) Observed waiting times (open symbols) and residence times (filled symbols), for state point II, at time intervals of  $1 t_i$  (black squares),  $2 t_i$  (red circles) and  $4 t_i$  (green triangles). (C) As in panel (B), but now for state point IV.

The measured and fitted (setting  $k_{max} = \infty$  and  $k_{min} = 0$ ) dynamic correlation functions of state points II and IV are shown in fig. 3(B). In colloidal systems capillary waves are in the overdamped regime [18,29] with a decay rate

$$\omega_k = \frac{1}{2t_c} (k\xi + (k\xi)^{-1}). \quad (7)$$

Here,  $t_c = \xi/u_c$  is the capillary time and  $u_c = \gamma/\eta$  is the capillary velocity with  $\eta$  the combined viscosities of the phases. From the fits, the interfacial tensions and the capillary times can be extracted, which gives  $t_c = 12$  s and  $\gamma = 69$  nN/m for state point II and  $t_c = 22$  s and  $\gamma = 25$  nN/m for state point IV. These values are comparable to those measured for similar systems in [18,31].

The residence and waiting times are calculated through the experimentally obtained functions  $p_n^\pm(h)$ . In order to check the possible variation of waiting and residence times, we calculate the distributions for intervals of 1, 2 and 4  $t_i$ . They are shown for state point IV at heights  $h = -1, 0$  and  $1 \langle h^2 \rangle^{1/2}$  in fig. 4(A). Note that the  $x$ -axis has intervals as units, not time. The distributions are clearly complicated: the shortest interval of 1 time interval becomes more dominant as  $\Delta t$  decreases as shown in the inset of fig. 4(A). On the other hand,  $h = -\langle h^2 \rangle^{1/2}$  has a surprisingly large interval of  $\approx 2-50$  interval durations, which occur most frequently for  $\Delta t = 4t_i$ . The longest

intervals decay exponentially and as expected decrease most rapidly in quantity for the largest time intervals. As a result, the waiting and residence times, shown for state points II and IV as a function of height in figs. 4(B) and (C), are confusing at first sight: if we increase the time in between observations  $\Delta t$  to 2 or 4  $t_i$ , the observed residence times are significantly larger!

**Interpretation and discussion.** – In order to understand these observations, we need some theoretical framework. In the spirit of von Smoluchowski we start with simple counting arguments, [2,3], in order to identify the essential object to be calculated. Consider a long measurement of  $N$  snapshots. We take pairs of consecutive heights and divide them into 4 sets:  $N^{++}(h)$  pairs where on both sides of the interval the interface is above  $h$ ,  $N^{+-}(h)$  pairs where the earlier value is above  $h$  and the later value below  $h$ ,  $N^{-+}(h)$  pairs where it is the other way round and finally  $N^{--}(h)$  pairs where the interface is on both sides of the interval below  $h$ . The first observation is that

$$N^{+-}(h) = N^{-+}(h) \equiv M(h), \quad (8)$$

since each interval in which the interface crosses the level  $h$  from above is followed by the next crossing from below. These numbers are also equal to the number of “hills”  $M(h)$ , which in turn is the same as the number of “valleys”. Now  $M(h)\tau^+(h)$  is the total length of the hills (measured in units  $\Delta t$ ). Thus, we have the relations

$$\begin{aligned} M(h)\tau^+(h) &= N^{++}(h) + M(h), \\ M(h)\tau^-(h) &= N^{--}(h) + M(h). \end{aligned} \quad (9)$$

We have to add  $M(h)$  on the right-hand side, since the number of points in a hill (valley) is one more than the number of intervals inside a hill (valley). Adding the two relations gives

$$\tau^+(h) + \tau^-(h) = \frac{N}{M(h)} \equiv \frac{1}{r(h)}. \quad (10)$$

$r(h)$  is the probability to find an interval where the interface crosses the level  $h$  from above to below  $h$ .

The second observation is that the right-hand side of (9) gives the probability to find a point above (below)  $h$ :

$$\frac{N^{++}(h) + M(h)}{N} = q^+(h) = \int_h^\infty dh' P_{eq}(h'), \quad (11)$$

$$\frac{N^{--}(h) + M(h)}{N} = q^-(h) = \int_{-\infty}^h dh' P_{eq}(h'), \quad (12)$$

which can be calculated from the equilibrium distribution and which states that the fraction of heights above or below  $h$  is equivalent to the fraction of time spent above or below height  $h$ . Thus, we find the expressions for  $\tau^\pm(h)$ ,

$$\tau^\pm(h) = \frac{q^\pm(h)}{r(h)}, \quad (13)$$

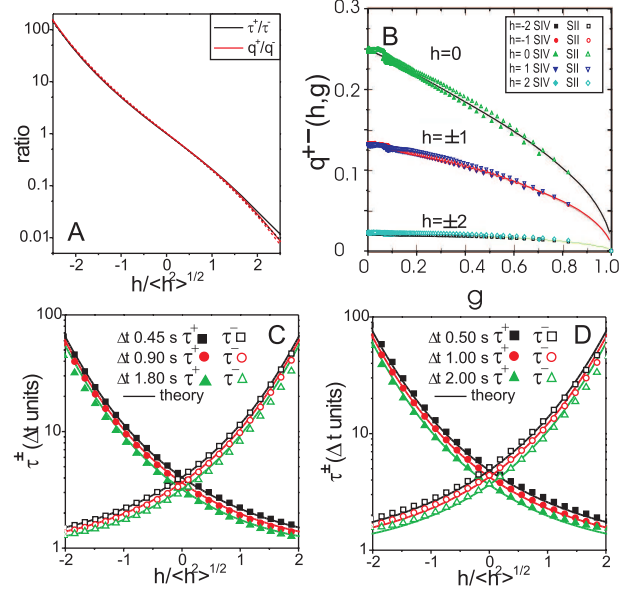


Fig. 5: (Colour on-line) Waiting and residence times for state points II and IV. (A) The relation  $q^+(h)/q^-(h) = \tau^+(h)/\tau^-(h)$  clearly holds over many orders of magnitude, both for state point II (dashed lines) and IV (solid lines). (B) The probability  $q^{+-}(h,g)$  as a function of  $g$  for  $|h|=0, 1$  and  $2$  ( $\langle h^2 \rangle^{1/2}$ ). The lines are the theoretical expressions, the symbols are obtained through the definition of  $r(h)$  from the experiment. (C) Theoretical and observed time intervals for the waiting and residence times of state point II, with  $\Delta t = 1$  (black squares), 2 (red circles) and 4 (green triangles)  $t_i$ . Open symbols are waiting times, closed symbols are residence times. The lines are the theoretical curves. (D) Theoretical and observed time intervals for state point IV, with  $\Delta t = 1, 2$  and  $4$   $t_i$ . Symbols are identical to those in panel (C).

showing that  $r(h)$  is the basic quantity to be calculated. Equation (13), independently of  $r(h)$ , implies

$$\frac{\tau^+(h)}{\tau^-(h)} = \frac{q^+(h)}{q^-(h)}, \quad (14)$$

which is experimentally verifiable. In fig. 5(A) we show that both sides of eq. (14) fall on a single master curve over nearly the full spectrum of heights for both state points.

For  $r(h)$  we need the joint probability to find the interface on level  $h'$  at  $t=0$  and on  $h''$  at time  $t$

$$\langle \delta(h(0,0) - h') \delta(h(0,t) - h'') \rangle = P_{eq}(h') G_c(h', 0|h'', t). \quad (15)$$

It is the product of the height distribution function  $P_{eq}$  and the conditional probability  $G_c$  for arriving at  $h''$  after a time  $t$ , starting from a height  $h'$  at  $t=0$ .  $G_c$  follows from the Langevin equation for the interface modes  $k$ , using a fluctuation force with a white-noise spectrum [32]. The result is

$$\begin{aligned} G_c(h', 0|h'', t) &= \frac{1}{[2\pi\langle h^2 \rangle (1 - g^2(t))]^{1/2}} \\ &\times \exp - \frac{[h'' - h'g(t)]^2}{2\langle h^2 \rangle [1 - g^2(t)]}, \end{aligned} \quad (16)$$

which is a universal result for Gaussian random variables and any  $g(t)$ . We point out that  $G_c$  contains only the correlation function  $g(t)$  and not explicitly the decay rate  $\omega_k$ . A check on (16) is that the correlation function  $\langle h(0)h(t) \rangle$  as calculated from (15) and (16) gives the result  $\langle h^2 \rangle g(t)$ . Figure 3(B) shows that  $g(t)$  is not exponentially decaying. Thus, the spatial process is non-Markovian [32]. In order to make the connection with  $r(h)$  we define the integral

$$q^{+-}(h, g) = \int_h^\infty dh' P_{eq}(h') \int_{-h}^h dh'' G_c(h', h''; g), \quad (17)$$

$q^{+-}$  translates to experiments as the fraction of subsequent height pairs  $h'$  and  $h''$  for which both  $h'' < h$  and  $h' > h$  are true.  $G_c(h', h''; g)$  is expression (16) with  $g(t)$  replaced by  $g$ . We have not found an analytical expression for this double integral, but its numerical evaluation is simple.  $q^{+-}$  curves for some values of  $h$  are plotted in fig. 5(B) as a function of the parameter  $g$ . The connection with  $r(h)$  is given by the relation  $r(h) = q^{+-}(h, g(\Delta t))$  where  $\Delta t$  is the sampling distance. In fig. 5(B) we have also plotted the experimental values of  $r(h)$  as constructed from its definition (10). For the sampling distance we may use any multiple  $m$  of the smallest interval  $t_i$ . Then the corresponding experimental point in fig. 5(B) is plotted for the value  $g = g(mt_i)$ . The agreement between the calculated  $q^{+-}(h, g)$  and the measured  $r(h)$  is remarkable. The observed residence and waiting times for  $\Delta t = 1, 2$  and  $4 t_i$  for state points II and IV, are shown in figs. 5(C) and (D) in terms of units  $\Delta t$ . Again we find excellent agreement with the theory, using the measured values for the  $g(t)$  function as theoretical input for the determination of  $r$ . Note that the  $y$ -axis has units “ $\Delta t$ ” and is dimensionless. In terms of time, the residence time at height  $h$  increases with  $\Delta t$ . Note that  $q^{+-}(h, g) = q^{+-}(-h, g)$ . Moreover, since  $q^+(h) = q^-(-h)$ , we have  $\tau^+(h) = \tau^-(-h)$ . Experimentally, we find that for large heights,  $\tau^-(-h)$  is always larger than  $\tau^+(h)$ , which may be an artifact of the method by which we determine the interfacial heights: small intensity fluctuations contribute more strongly to the tanh fit in the gas phase than in the liquid phase. In fig. 2(C) this shows up as more speckly noise for the high intensities of the liquid phase. On the other hand, the high degree of symmetry is remarkable in view of a viscosity of the liquid phase that is roughly ten times higher than that of the gas, as can be estimated from the sedimenting liquid and gas droplets in the late stages of phase separation. At sufficiently large  $h$ , the theoretical times are always larger than the experimental values, see figs. 5(C) and (D). This is at least partly due to the limited amount of time points considered, which tends to exclude the tail of the distributions  $p_n^\pm(h)$ .

We now ask ourselves the question whether we can take the limit of  $\Delta t \rightarrow 0$  and arrive at a continuum description. If  $r(h, \Delta t)$  were to shrink proportional to  $\Delta t$ , the  $\tau^\pm(h)$  would increase inversely proportional to

$\Delta t$ . From a continuum description one would expect the relations

$$T = \lim_{\Delta t \rightarrow 0} \tau^+(h) \Delta t, \quad \Theta = \lim_{\Delta t \rightarrow 0} \tau^-(h) \Delta t \quad (18)$$

and  $T$  and  $\Theta$  would have a finite limit. However, analyzing the small  $\Delta t$  behavior of expression (17), which amounts to the limiting behavior for  $g(\Delta t) \rightarrow 1$ , we find

$$q^{+-}(h, g \rightarrow 1) \simeq \frac{\sqrt{1-g}}{\pi\sqrt{2}} \exp\left[-\frac{h^2}{2\langle h^2 \rangle}\right]. \quad (19)$$

The square root in (19) is a reflection of the Brownian character of the fluctuations. If the initial decay of  $g(t)$  is linear,  $r(h)$  vanishes as  $(\Delta t)^{1/2}$  and consequently  $T$  and  $\Theta$  vanish. Clearly, our results are only applicable to mesoscopic time scales, for which we may use the Langevin equation, and will therefore break down at the time scale of Brownian solvent molecule collisions. This would show up in a measurement of the decay of  $g(t)$  on these times scales, which are presently unreachable experimentally. Moreover, the capillary-wave decay rates as given in (7) do not apply to these microscopic time scales.

With eq. (12) and the computation of  $q^{+-}(h, g)$  we have determined the residence and waiting times without evaluating the distributions  $p_n^\pm(h)$ . The latter quantities can also be calculated using multiple correlation functions, which are generalizations of eq. (15). Their evaluation is increasingly involved, due to the non-Markovian character of the spatial process. Experimentally, the exhaustive amount of multiple correlation functions can be determined given sufficient time points, analogous to the results in fig. 5(B). Furthermore, predictions for the occurrence of a fluctuation of height  $h$  in a finite area  $A$  are feasible with algorithms similar to those presented here, but involving the positional correlation function as well. Interestingly, the positional cutoff is of the order of the particle diameter and therefore within experimental reach. We leave these aspects for a further study.

**Conclusion.** – We have presented confocal microscopy experiments along with theory for the microscopic waiting and residence times of heights  $h$  of the capillary waves of the fluid-fluid interface of a phase-separated colloid-polymer mixture. Due to the Brownian character of the process, these times depend on the experimental measurement interval  $\Delta t$ . The results from this discrete time sampling are predictable in terms of the decay of the height-height correlation function  $g(t)$ . The theory is essentially divided into two parts: the computation of  $g(t)$  from the parameters capillary time and interfacial tension and the determination of  $G_c$  from  $g(t)$ . In this letter we concentrated on the latter part. We found excellent agreement between experiments and theory.

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