

Unidirectional Droplet Propulsion onto Gradient Brushes Without External Energy Supply

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Abstract

Using extensive molecular dynamics simulation of a coarse-grained model, we demonstrate the possibility of sustained unidirectional motion (durotaxis) of droplets without external energy supply when placed on a polymer brush substrate with stiffness gradient in a certain direction. The governing key parameters for the specific substrate design studied, which determine the durotaxis efficiency, are found to be the grafting

density of the brush and the droplet adhesion to the brush surface, whereas the strength of the stiffness gradient, the viscosity of the droplet or the length of the polymer chains of the brush have only minor effect on the process. It is shown that this durotaxial motion is driven by the steady increase of the interfacial energy between droplet and brush as the droplet moves from softer to stiffer parts of the substrate whereby the mean driving force gradually declines with decreasing roughness of the brush surface. We anticipate that our findings indicate further possibilities in the area of nanoscale motion without external energy supply.

INTRODUCTION

The motion of nano-objects, for example, liquid nanodroplets, can be provoked and sustained on solid substrates without an external energy supply. Moreover, the direction of motion can be controlled and nanodroplets can move along predetermined trajectories. A way of achieving this effect is by placing the droplet onto a *gradient* substrate, that is, a substrate with a steadily varying property along a specific direction. This is particularly attractive for the development of various technologies in microfluidics, microfabrication, coatings, nanoscale actuation and energy conversion, and biology.^{1–12} Various possibilities for the design of gradient substrates have been reported. For example, durotaxis motion is caused by changes in stiffness along a substrate, as has been shown in various natural processes in biology (*e.g.*, cell movement on tissues)^{11,12} and in the case of real and *in silico* experiments with liquid droplets.^{13–23} Another characteristic example is the rugotaxis motion of droplets on wavy substrates with a gradient in the wavelength that characterises their pattern.^{24,25} Other possibilities include the use of wettability differences^{26,27} and physical pinning.²⁸ Recent work has also highlighted the possibility of uni-directional transport of small condensate droplets

on asymmetric pillars²⁹ or three-dimensional capillary ratchets.³⁰ In the latter case, the motion can take place in one or the other direction, depending on the surface tension of the liquid. Other possibilities of directional motion can take advantage of charge gradients that can achieve long-range transport and are based on electrostatic^{31,32} or triboelectric charges.³³ In contrast, motion caused by temperature gradient (thermotaxis),³⁴ electrical current,^{35–38} charge,^{39–41} or even simple stretch,⁴² would require external energy supply,¹⁹ as, also, in the case of chemically driven droplets,^{43,44} droplets on vibrated substrates^{45–48} or wettability ratchets.^{49–52}

Inspired by our previous work with specific substrate designs that lead to the durotaxis¹³ and rugotaxis²⁴ motion of nanodroplets as motivated by the corresponding experiments,^{15,25} here, we propose a new design for the substrate, which is capable of sustaining the droplet motion. We consider a polymer brush, consisting of polymer chains grafted onto a flat, solid surface, and the stiffness gradient is introduced to the brush substrate by varying the stiffness of the polymer chains, which in practice amounts to tuning their persistence length. To understand the mechanism of the durotaxis motion on brush substrates and analyse the influence of relevant parameters for the brush and the droplet (*e.g.*, droplet adhesion to the substrate, droplet size, viscosity, *etc.*), we have carried out extensive molecular dynamics (MD) simulations of a coarse-grained (CG) model. This is crucial as the nanoscale motion of nano-objects is usually controlled by tiny effects at the interface between the droplet and the substrate resulting from the molecular interactions between the two, which only a method with molecular scale resolution can capture. As in the case of durotaxis¹³ and rugotaxis²⁴ motions, we find that the motion is caused by a gradient in the droplet–substrate interfacial energy, which translates into an effective force that drives the droplet towards the stiffer, flatter parts of the substrate. Moreover, we find that the efficiency of the durotaxis motion for brush substrates is higher for moderate values of the grafting density and droplet adhesion to the substrate as well as for smaller droplets and longer brush chains. Surprisingly, we have not observed a significant effect of the stiffness gradient in the case of brush sub-

strates when the motion was successful. We anticipate that our study will shed some light into the durotaxis motion of droplets on brush, gradient substrates, thus providing further possibilities in nanoscale science and technology,²⁰ for various medicine and engineering applications.^{12,53} Moreover, brush substrates share connection with various biological surfaces that expel various exogenous substances from their structure,⁵⁴ such as the mucus layer from airway epithelia,⁵⁵ while the gradient concept plays an important role in applications of regenerative medicine.¹² In the following, we discuss our simulation model and methodology. Then, we will present and discuss our results, and in the final section we will draw our conclusions.

MATERIALS AND METHODS

Our system consists of a polymer-brush substrate and a droplet placed on its soft part (Fig. 1). We have found that the durotaxis motion in the case of brush substrates takes place from the softer towards its stiffer parts, which is in line with previous simulation findings for another substrate design with stiffness gradient.¹³ In the direction of the stiffness gradient, the substrate has length, $L_x = 100 \sigma$ (σ is the unit of length), while in the y -direction, $L_y = 50 \sigma$, which guarantees that mirror images of the droplet in this direction will not interact during the course of the simulation due to the presence of periodic boundary conditions that are applied in all Cartesian directions. Finally, two walls are placed normal to the x direction as shown in Fig. 1 and the size of the box in the x direction is large enough to guarantee that there are no interactions between the walls or the polymers on the two opposite sides of the simulation domain in the x direction. Wall beads were kept immobile during the simulation.

The standard bead–spring model⁵⁷ has been employed in our simulations. In this model, interactions between any of the system components, *i.e.* the drop (d), the brush (b), and

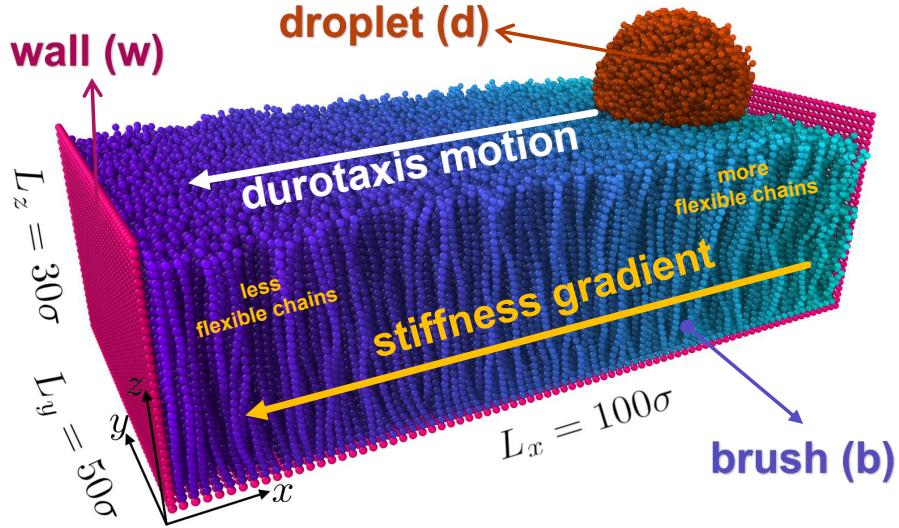


Figure 1: Typical initial configuration of the system, where the droplet is placed on the softest end of the brush substrate. Here, $N_b = 30$, $N = 4000$, and $N_d = 10$ beads, $\sigma_g = 0.6 \sigma^{-2}$, and $\varepsilon_{db} = 0.6 \epsilon$. At the softest end $k_\theta = 0 \epsilon/\text{rad}^2$, while at the stiffest end $k_\theta = 80 \epsilon/\text{rad}^2$, with a linear gradient of k_θ between them in the x direction. L_x , L_y , and L_z , indicate the dimensions of the immobile walls. See text for further details. The snapshot of the system was obtained using Ovito software.⁵⁶

the wall (w) beads, are described by means of the Lennard-Jones (LJ) potential

$$U_{\text{LJ}}(r) = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^6 \right], \quad (1)$$

where r is the distance between any pair of beads in the system within a cutoff distance. Indices i and j in Eq. 1 indicate the type of beads. The size of the beads is $\sigma_{ij} = \sigma$ for all interactions. The LJ potential is cut and shifted at the cutoff distance, $r_c = 2.5 \sigma$, for the interaction between the droplet (d) beads, as well as the interaction between the droplet and the brush (b) beads. In contrast, a purely repulsive potential for the interaction between the brush beads, as well as between the brush and the wall (w) beads, was considered, that is, in this case, $r_c = 2^{1/6} \sigma$. The strength of the attractive interactions is determined by the parameter ε_{ij} of the LJ potential⁵⁸. In our study, $\varepsilon_{dd} = 1.5 \epsilon$, with ϵ defining the energy scale. Moreover, $\varepsilon_{bb} = \epsilon$, while ε_{db} is the parameter that controls the attraction (adhesion)

of the droplet to the substrate beads and in our study ranged from 0.1 to 1.2 ϵ .

The grafting density, σ_g , is varied from 0.1 to 1.0 σ^{-2} in our study. The size of the droplets can also vary through the total number of beads that the droplet contains, which ranged between 2×10^3 and 1.6×10^4 beads in our simulations. These beads belong to fully flexible, linear polymer chains. By varying the length of the droplet chains, e.g., from 10 to 80 beads, we can alter the viscosity of the droplet.¹³ The finite extensible nonlinear elastic (FENE) potential⁵⁷ was used to tether together consecutive beads in these polymer chains, as well as the polymer beads along the linear brush-polymer chains. The mathematical expression for the FENE potential is as follows:

$$U_{\text{FENE}}(r) = -0.5K_{\text{FENE}}R_0^2 \ln \left[1 - \left(\frac{r}{R_0} \right)^2 \right], \quad (2)$$

where r is the distance between two consecutive beads along the polymer backbone, while $R_0 = 1.5 \sigma$ expresses the maximum extension of the bond, and $K_{\text{FENE}} = 30 \epsilon/\sigma^2$ is an elastic constant. Lengths of the polymer chains in the droplet greater than $N_d = 10$ guarantee that there are no evaporation effects and the vapour pressure is hence sufficiently low⁵⁹. We have also investigated the effect of the length, N_b , of the polymer chains of the brush on the durotaxis motion, by choosing different lengths, namely $N_b = 15, 30$, and 50 beads.

The stiffness gradient is imposed on the brush substrate by varying the stiffness of the individual brush polymer-chains. The total length of the brush chains, N_b , was the same for all chains, but their stiffness changed depending on the Cartesian coordinate of their grafting site in the x direction, *i.e.* chains with the same position X of their grafted end have the same stiffness. The chain stiffness was controlled by using a harmonic angle potential for every triad of consecutive beads along the polymer chain and tuning its strength through the harmonic constant k_θ . The form of the harmonic potential reads:

$$U_{\theta_{ijk}}(\theta) = k_\theta(\theta_{ijk} - \theta_0)^2, \quad (3)$$

where θ_{ijk} is the angle between three consecutive beads i, j, and k along a brush polymer chain and, $\theta_0 = \pi$ rad, is the equilibrium angle. A linear gradient in the stiffness constant, k_θ , is considered in our study to explore the properties of our systems. As we will discuss later, while the gradient in the stiffness of the substrate is necessary to initiate and maintain the durotaxis motion, the system is rather insensitive to the exact value of the gradient and the key parameters for the brush substrate turn out to be the grafting density, σ_g , and the substrate wettability as controlled via the parameter ε_{db} . The reasons for this will be revealed during the discussion of our results.

To evolve our system in time, the Langevin thermostat was used, whose details have been discussed in previous studies^{60,61}. Hence, the simulations are in practice realised in the canonical ensemble,⁶² where the temperature, T , of the system fluctuates around a predefined value $T = \epsilon/k_B$, with k_B being the Boltzmann constant and ϵ the energy unit. For the integration of the equations of motion, the LAMMPS package⁶³ was employed. The MD time unit is $\tau = \sqrt{m\sigma^2/\epsilon}$, where m is the unit of mass, and the integration time step was $\Delta t = 0.005 \tau$. Typical simulation trajectories start from configurations like the one presented in Fig. 1 with the total length of each trajectory being 10^8 MD integration steps. If a droplet fully transverses the substrate from the softest to the stiffest end of the substrate, then the durotaxis motion is considered as successful. To ensure reliable statistics an ensemble of ten independent trajectories with different initial conditions (by changing the initial velocities assigned to each particle) was used for each set of system parameters. Our results are based on the analysis of these trajectories for each case.

RESULTS AND DISCUSSION

By exploring a wide range of parameters, we have found that the grafting density, σ_g , and the attraction strength between the droplet and the substrate, ε_{db} , are two key parameters of the substrate design, since they greatly affect the possibility for successful durotaxis. Figure 2

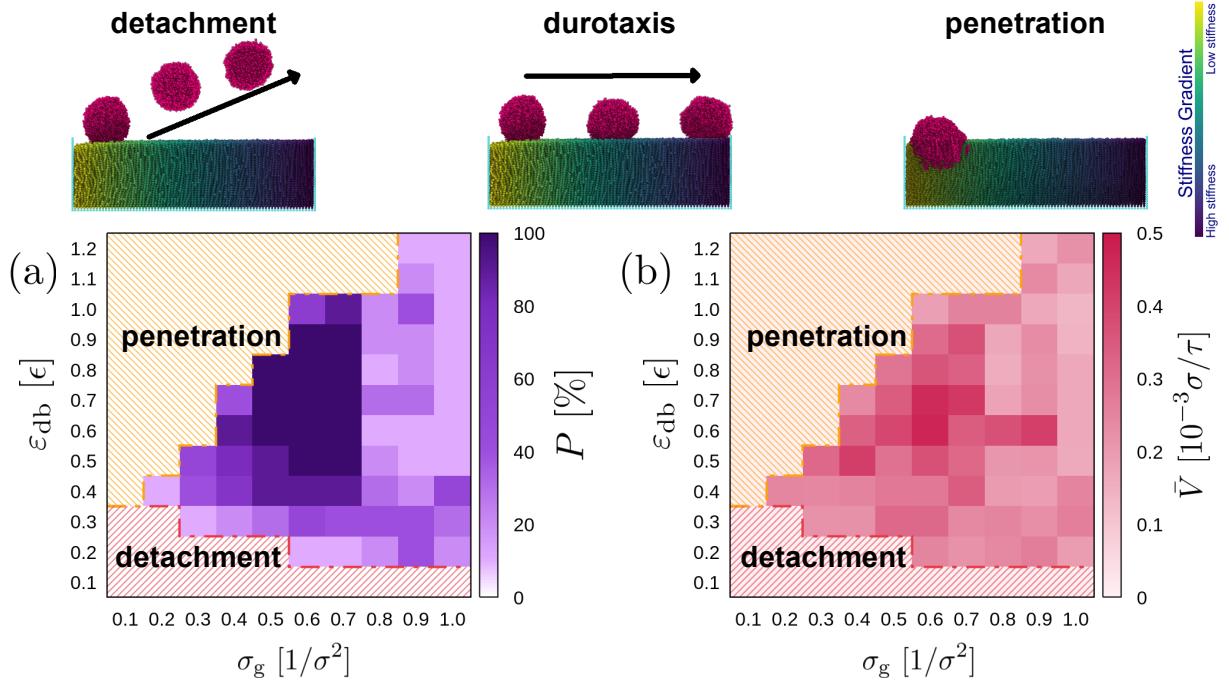


Figure 2: (a) Regime map indicating the probability, P (color scale), that a droplet will cover the full distance over the substrate in the x direction from the softest to the stiffest part (successful durotaxis cases) for different values of the droplet–substrate attraction, ε_{db} , and the grafting density, σ_g . Probabilities, P , are based on an ensemble of ten independent simulations for each set of parameters. The regimes where the droplet penetrates into the brush or detaches from the substrate due to the weak ε_{db} attraction are also shown with a different color. (b) The color map indicates the average velocity of the droplet, $\bar{v} = L'_x/t$, for the successful durotaxis cases, where t is the time that the droplet needs to cross the full length of the brush substrate in the x direction, and L'_x is the actual distance covered by the centre-of-mass of the droplet for each successful case. $N = 4000$, $N_d = 10$, $N_b = 30$ beads. The stiffness constant for the polymer chains in the softest part of the substrate is zero (fully flexible chains), growing linearly to $k_\theta = 80 \epsilon/\text{rad}^2$ at the stiffest part of the substrate. Since $L_x = 100 \sigma$, the stiffness gradient is $\Gamma = 0.8 \epsilon/\text{rad}^2\sigma$. Snapshots on top of the plot indicate examples of detachment, durotaxis, and penetration, as indicated.

presents the regime maps as a function of these two parameters with the probability, P , of successful durotaxis calculated from the ensemble of ten independent simulations for each set of parameters. However, in our *in silico* experiments, apart from durotaxis motion, we have also documented situations in which the droplet penetrates into the substrate or detaches from it. Our results indicate that small attraction strengths will lead to droplet detachment. This is more probable at smaller grafting densities due to fewer brush–droplet interactions. In contrast large values of the attraction strength, ε_{db} , can lead to the penetration of the

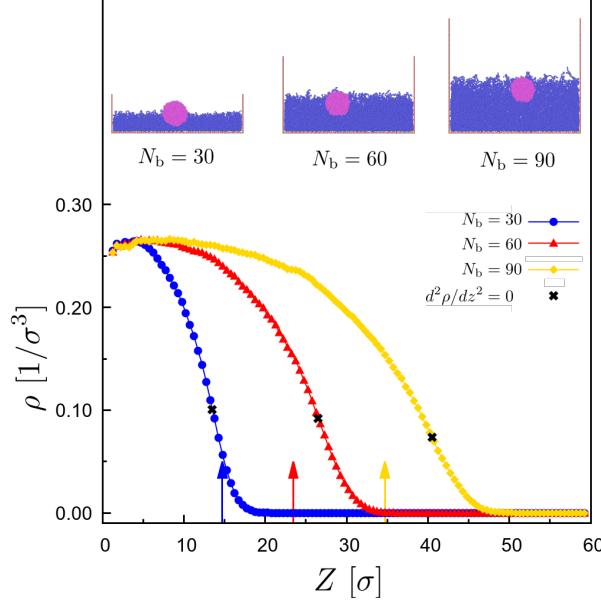


Figure 3: Density profile in the z direction for three polymer brushes at $\sigma_g = 0.6 \sigma$ with fully flexible chains of length, $N_b = 30, 60$, and 90 beads, as indicated. The inflection point of the curves, $d^2\rho/dz^2 = 0$, marked with \times , is shown for each case, which corresponds to the height of the brush. The position of the centre of mass of the droplet in the z direction is marked with arrows of the same colour for each case. Here, $N = 4000$ and $N_d = 10$ beads, and $\varepsilon_{db} = 0.6 \epsilon$. Snapshots for each case are shown in the plot. In the case of brushes with longer chains, the droplet is immersed deeper into the brush.

brush substrate by the droplet, again for smaller values of the grafting density, σ_g . Moreover, our results suggest that the difficulty of the droplet to penetrate into the substrate increases roughly linearly with the grafting density up to $\varepsilon_{db} = \epsilon$, as evidenced by the linear boundary in the regime maps. In fact, penetration becomes impossible when $\sigma_g \geq 0.9 \sigma^{-2}$, since there is not enough space among the brush beads to accommodate additional droplet beads. Moreover, the degree of brush penetration also depends on the length, N_b , of the brush chains, as shown in Fig. 3. In general, our data suggest that droplets are immersed deeper in brushes with longer chains, as shown here in the case of fully flexible polymers and judging by the centre-of-mass of the droplet with respect to the position of the brush surface, as defined by the inflection point at the density profile (Fig. 3). A more detailed study on this effect could potentially reveal more details for droplets immersed in brush substrates, but this clearly goes beyond the scope of our current study.

When penetration and detachment of the droplet are avoided, then persistent durotaxis motion is observed with a certain probability, P , which depends on the choice of σ_g , and ε_{db} (Fig. 2a). From the results of Fig. 2a, we find that the range $0.5 \sigma^{-2} \leq \sigma_g \leq 0.7 \sigma^{-2}$ combined with $0.5 \epsilon \leq \varepsilon_{\text{db}} \leq 0.9 \epsilon$, in general, provides certainty in the success of the durotaxis motion ($P = 100 \%$), since all our droplets were able to fully cross the substrate from the softest to the stiffest parts of the brush within the available simulation time of 10^8 MD time steps. As the grafting density increases above $0.7 \sigma^{-2}$, however, we observe that the probability of durotaxis success suddenly decreases. In this case, a higher density of the brush chains increases the resultant brush stiffness owing to the close packing of the chains, which leads to a situation that the role of the nominal stiffness of the individual brush chains, k_θ , in determining the effective stiffness gradient becomes negligible. As we will see later in our discussion concerning the underlying durotaxis mechanisms, the extent of disarray of the brush chain end-monomers at the brush surface is also reduced pointing to a rather flat density profile.

To determine the efficiency of the durotaxis motion, we have computed the average velocity, \bar{v} , of the droplet for the successful cases for each set of parameters σ_g and ε_{db} (Fig. 2b). Our results indicate that the probability, P , for success rather correlates with the highest average velocity, \bar{v} , but large values of \bar{v} can also be obtained in certain cases where $P < 100 \%$, for example, the case $\sigma_g = 0.9 \sigma^{-2}$, $\varepsilon_{\text{db}} \sim 0.6 \epsilon$ (Fig. 2b). This is a clear indication that durotaxis motion is controlled by tiny effects that can greatly influence the outcome of the experiments. Moreover, obtaining reliable statistics in cases of $P < 100\%$ remains a challenge in MD since this would require the realisation of a large number of simulations. Hence, as $P \rightarrow 0$ obtaining reliable statistics becomes more of a challenge and outliers in the statistics are more probable. In summary, the plots of Fig. 2 suggest that if one would like all droplets to fully cross the substrate in the direction of the stiffness gradient in the shortest time, then values of $\sigma_g = 0.6 \sigma^{-2}$ and $\varepsilon_{\text{db}} \approx 0.7 \epsilon$ would constitute an optimal choice in the *in silico* experiments. Hence, we argue that moderate values of σ_g and

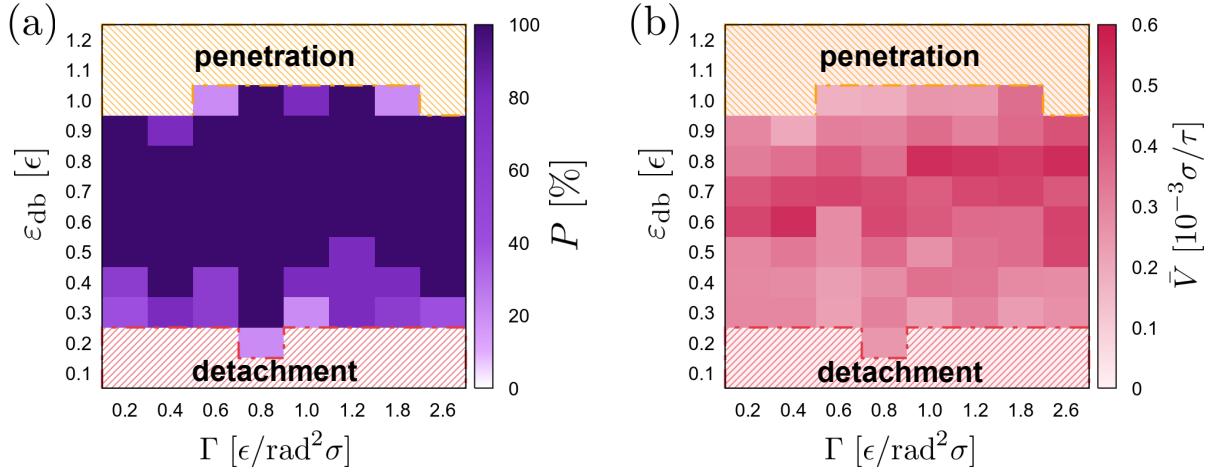


Figure 4: (a) Regime map indicating the probability, P (color scale), that a droplet will cover the full distance over the substrate in the x direction from the softest to the stiffest part (successful durotaxis cases) for different values of the droplet–substrate attraction, ε_{db} , and the stiffness gradient $\Gamma = dk_\theta/dx$. The regimes where the droplet penetrates into the brush or detaches from the substrate due to the weak ε_{db} attraction are also shown with a different color. (b) The color map indicates the average velocity of the droplet, $\bar{v} = L'_x/t$, for the successful durotaxis cases, where t is the time that the droplet needs to cross the full length of the brush substrate in the x direction, and L'_x is the actual distance covered by the centre-of-mass of the droplet for each successful case. The stiffness constant, k_θ , for the polymer chains in the softest part of the substrate is zero (fully flexible chains), growing linearly to its highest value at $x = L_x = 100 \sigma$, which depends on the chosen stiffness gradient, Γ . Here, $\sigma_g = 0.6 \sigma^{-2}$, $N = 4000$, $N_b = 30$, and $N_d = 10$ beads.

ε_{db} favour successful and efficient (in terms of time to cross the whole substrate) durotaxis motion.

Finally, we have explored the effect of the stiffness gradient on the durotaxis motion. Here, we have picked the best case of Fig. 2, that is $\sigma_g = 0.6 \sigma^{-2}$ and $\varepsilon_{\text{db}} = 0.6 \epsilon$, and varied the stiffness gradient $\Gamma = dk_\theta/dx$ in the range 0.2–2.6 for fully flexible chains at the softest part of the substrate, which has actually provided the best result in terms of durotaxis success and efficiency. Overall, we have found that durotaxis is insensitive to the value of Γ in the range $0.5 \epsilon \leq \varepsilon_{\text{db}} \leq 0.9 \epsilon$ (Fig. 4a), in contrast to what has been observed for other *in silico* substrate designs.¹³ Moreover, the average velocities are spread out with small variations and no indication of a clear trend (Fig. 4b) that would indicate that a larger stiffness gradient would lead to more efficient durotaxis motion exists, which has been

the case for other substrate designs.¹³ Moreover, since the motion is most efficient when the softest part consists of fully flexible chains ($k_\theta = 0 \text{ } \epsilon/\text{rad}^2$) might suggest that brush substrates with polymer chains of small persistence lengths (as soft as possible) are more suitable for successful durotaxis motion. Henceforth, all our results refer to brush substrates with fully flexible chains at their softest part and stiffness gradient $\Gamma = 0.8 \text{ } \epsilon/\text{rad}^2\sigma$.

In the following, we examine the effect of various parameters on the efficiency of the durotaxis motion. For our analysis, we have picked the case $\sigma_g = 0.6 \sigma^{-2}$, which has shown the best performance in terms of the probability, P , and the average velocity, \bar{v} , in our study (Fig. 2) and therefore would most probably allow for exploring a wider range of the parameter space. Then, Figs 5a,d illustrate the dependence of the average velocity, \bar{v} , on the attraction strength, ε_{db} , for various droplet sizes, N . We observe that the fastest durotaxis motion takes place for the smallest droplets, namely $N = 2000$ beads. As ε_{db} increases, a maximum value of the average velocity, \bar{v} , appears for each case with droplets of different size. In addition, we consistently see that this maximum value of \bar{v} becomes smaller for larger droplets. For example, for the droplet of $N = 2000$ beads the average velocity measured over ten trajectories is $\bar{v} \approx 4.7 \times 10^{-4} \text{ } \sigma/\tau$, while $\bar{v} \approx 3.5 \times 10^{-4} \text{ } \sigma/\tau$ for droplets with 16000 beads. These differences are generally considered small, especially compared to other *in silico* experiments.^{13,24} Moreover, we see that the maximum shifts to higher values of the attraction strength, ε_{db} , as the size of the droplet increases. For example, the maximum velocity is observed when $\varepsilon_{\text{db}} = 0.4 \epsilon$ for droplets with $N = 2000$ beads and for $\varepsilon_{\text{db}} = 0.9 \epsilon$ for droplets of 16000 beads (Fig. 5d). Finally, for small droplets we observe a steep increase of the average velocity with ε_{db} , and then a slow decrease (Fig. 3a). For medium-size droplets, (*i.e.* $N = 4000$ and $N = 8000$ beads), there is a smooth maximum that develops in the middle range of ε_{db} , *i.e.* $0.6 \epsilon \leq \varepsilon_{\text{db}} \leq 0.7 \epsilon$, while in the case of droplets with $N = 16000$ beads there is a maximum that slowly develops as ε_{db} increases, which is followed by a steeper decrease when $\varepsilon_{\text{db}} > 0.9 \epsilon$. In summary, we observe that the size of the droplets is an important parameter for the durotaxis motion.

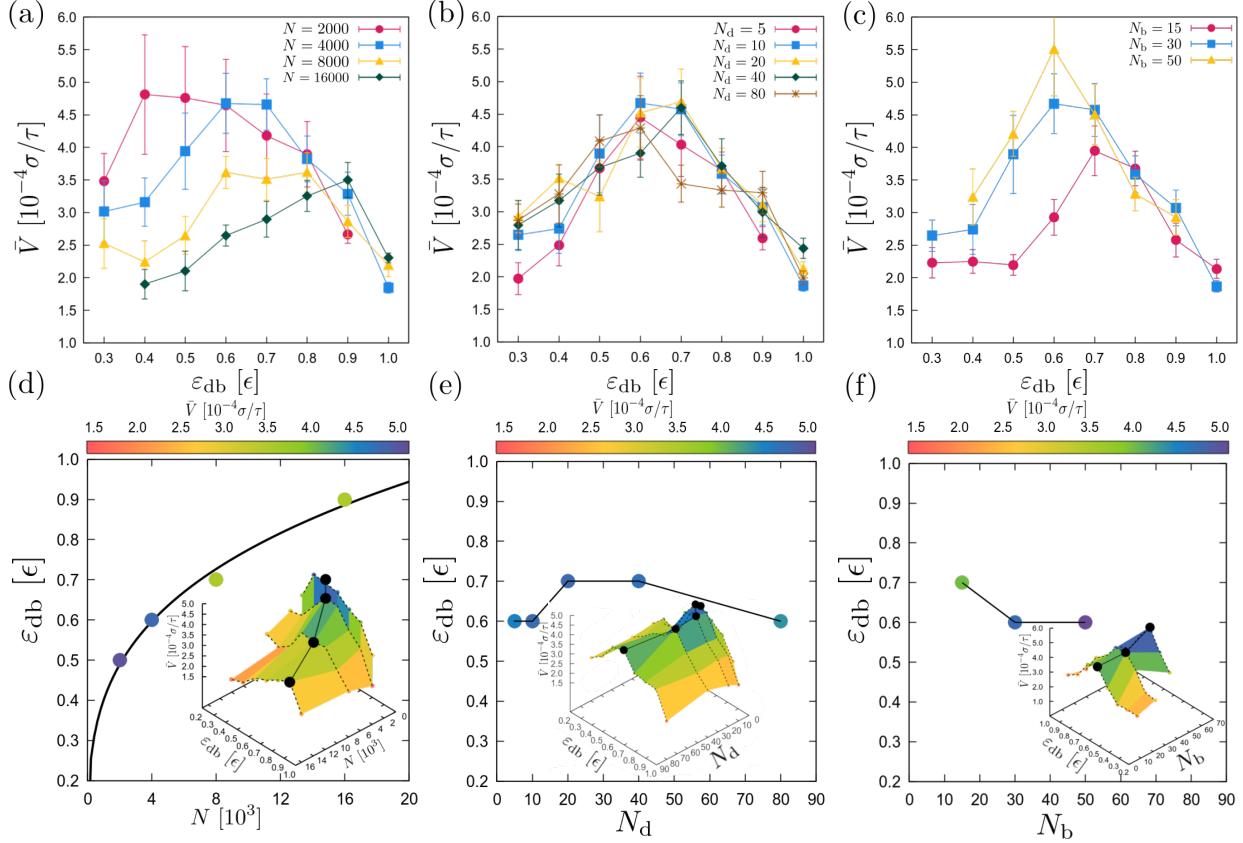


Figure 5: Average droplet velocity, \bar{v} , as a function of ε_{db} for different (a) droplet size, N ($N_d = 10$, $N_b = 30$ beads), (b) chain length of the polymer chains of the droplet, N_d ($N = 4000$ and $N_b = 30$ beads), and (c) brush polymer chain length, N_b ($N = 4000$ and $N_d = 10$ beads), as indicated. (d) Documented maximum average velocity, \bar{v} , indicated by the colour map, as a function of ε_{db} and N . Inset shows the average velocity, \bar{v} , for all pairs of (ε_{db}, N) . The black points indicate the pairs (ε_{db}, N) for which we have the maximum average velocity, \bar{v} , which is shown in the main plot. (e) Same as (d), but data are plotted as a function of (ε_{db}, N_d) . (f) In this case data are plotted as a function of (ε_{db}, N_b) . $\sigma_g = 0.6 \sigma^{-2}$, $\Gamma = 0.8 \epsilon/\text{rad}^2\sigma$ in all cases. Panels (a-c) here show data as a function of ε_{db} with one other quantity varying, the others held constant. Therefore, it does take care to carry out a systematic study with as much held constant between data as useful. Panels (d-f) visualize the same data as in the top panels but with a different visualization in terms of maximum velocities.

The next parameter to examine is the chain length, of the polymers comprising the droplet, N_d (Figs 5b, e). In practice, longer chain lengths would result in a larger droplet viscosity. During this and previous work with polymer liquid-droplets¹³ we have determined that the most relevant values for our study are within the range $10 \leq N_d \leq 80$ beads. Interestingly, the droplet viscosity seems not to play an important role in the overall efficiency

of the durotaxis motion, for a given attraction strength, ε_{db} . In other words, droplets with different N_d would exhibit a similar durotaxial efficiency for a specific choice of ε_{db} . As a result, the maximum average velocity, \bar{v} , as a function of ε_{db} appears at $\varepsilon_{\text{db}} \sim 0.6 - 0.7 \epsilon$ (Fig. 5e). Hence, we can conclude that droplets with different viscosity will have a similar durotaxis performance and, here, a moderate choice for the value of droplet–substrate attraction strength would yield the fastest durotaxis motion.

The effect of the length of the brush chains, N_b , on the durotaxis motion is shown in Figs 5c, f. We find that the larger the length, N_b , the more efficient the durotaxis motion becomes. Although a larger difference is noticed when N_b was doubled from 15 to 30 beads, a saturation in our data occurred when N_b increased from 30 to 50 beads. Overall, our results indicate that brushes with longer polymer chains favor the durotaxis motion. Moreover, for $N_b = 30$ and 50 beads, the maximum velocity is found for $\varepsilon_{\text{db}} = 0.6 \epsilon$, and hence is independent of the choice of N_b . The reasons for this behavior will become more apparent as we will discuss the underlying mechanism of the droplet motion in the following.

From our earlier studies, we have seen that the minimization of the interfacial energy, U_{db} , between the droplet and the substrate is the driving force for the durotaxis motion in the case of substrates with stiffness gradient¹³ or wrinkle substrates with a gradient in the wavelength characterising the wrinkles.²⁴ This has also been found in the case of a nanoflake on substrates with stiffness gradient.¹⁶ Moreover, we have argued that the efficiency of the motion depends on the rate of change of the interfacial energy along the gradient direction. Hence, it is relevant to examine the interfacial energy, U_{db} , as a function of time, t , and the coordinate, X , of the centre-of-mass of the droplet along the substrate (see Fig. 6 showing these quantities for a successful durotaxis case). Our results indicate that U_{db} over time reaches more negative values (Fig. 6a), which corresponds to a larger number of attractive pair interactions between the droplet and the substrate. Importantly, we also see that the energy decreases as a function of the position of the droplet, X , which clearly indicates that the droplet moves to areas of more negative energy (Fig. 6b) towards the stiffer parts of

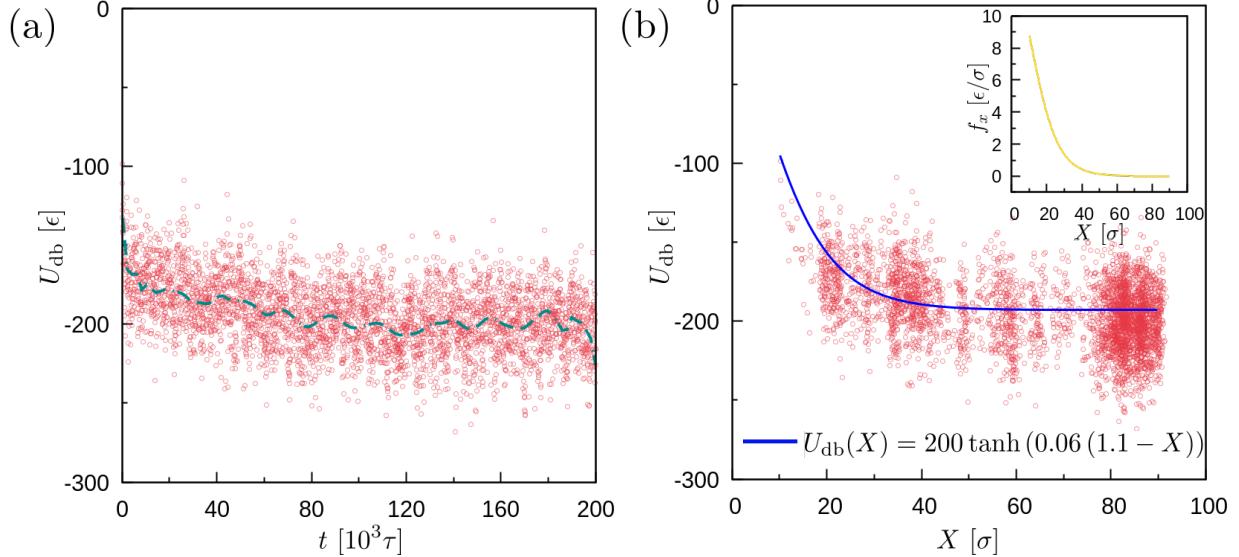


Figure 6: Droplet–brush interfacial energy, U_{db} , as a function of time, t (a, dashed line is a guide for the eye), and the position, X , of the centre of mass of the droplet in the x direction (b), for a case with successful durotaxis ($N = 4000$, $N_d = 10$, and $N_d = 30$ beads. $\varepsilon_{\text{db}} = 0.6 \epsilon$ and $\sigma_g = 0.6 \sigma^{-2}$). Inset shows the force, $f_x = -\frac{\partial U_{\text{db}}}{\partial x}$ based on a nonlinear fit of the tanh function on the U_{db} data. The higher concentration of points in panel (b) at certain ranges of X simply indicates that the droplet spends more time at these positions as it moves to the stiffer parts of the substrate. The fit function of the U_{db} only provides an average picture of the decay of the interfacial energy.

the substrate (increasing X). A larger decrease of the energy takes place in the initial soft parts of the substrate at small X values, while the change in the substrate–droplet interfacial energy is smaller after the droplet has moved a distance about 40σ . Moreover, we can see that the droplet does not spend the same time at each position X , as seen by the density of points at certain positions, X , and knowing that samples have been taken over time at equal intervals. Hence, the durotaxis motion of the droplet cannot be characterised as a steady state. To illustrate the effect of the gradient in the interfacial energy, U_{db} , one can actually plot the negative derivative of the interfacial energy (inset of Fig. 6b) after performing a suitable fit on the U_{db} . This derivative would correspond to an on-average driving force $f_x = -\frac{\partial U_{\text{db}}}{\partial x}$ that propels the droplet toward the stiffer parts of the brush substrate. It is clear that this ‘force’ becomes significantly smaller when the droplet enters the stiffer half of the substrate in the x direction. However, this small ‘force’ is still able to sustain the

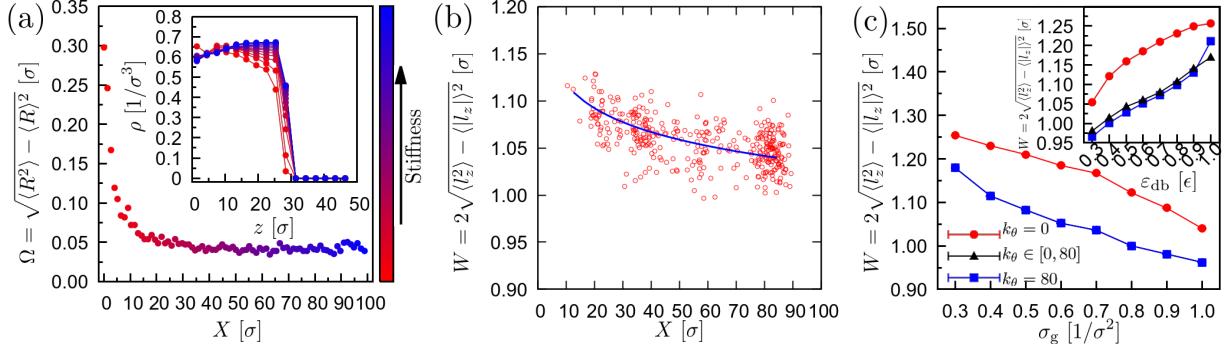


Figure 7: (a) The standard deviation in the end-to-end distance of the brush polymer chains as a function of their grafting position, X . Larger values of X correspond to the stiffer parts of the substrate. Inset shows the density profile in the z direction at different positions, X . The colour reflects the stiffness of the chains (k_θ). $\varepsilon_{db} = 0.6 \epsilon$, $\sigma_g = 0.6 \sigma^{-2}$. $\Gamma = 0.8 \epsilon/\text{rad}^2\sigma$ and initial stiffness $0 \epsilon/\text{rad}^2$ at the softest end. $N = 4000$, $N_d = 10$, $N_b = 30$ beads. (b) Interpenetration length, W . l_z is the average distance of contact pairs between the droplet and the brush for the same set of parameters as in (a) with X here indicating the centre-of-mass position of the droplet in the x direction along the gradient. (c) Average interpenetration length as a function of the grafting density, σ_g , for substrates with constant stiffness ($k_\theta = 0 \epsilon/\text{rad}^2$ or $k_\theta = 80 \epsilon/\text{rad}^2$) or with stiffness gradient $\Gamma = 0.8 \epsilon/\text{rad}^2\sigma$ and initial stiffness $0 \epsilon/\text{rad}^2$ at the softest end, as indicated. $N = 4000$, $N_d = 10$, $N_b = 30$ beads. $\varepsilon_{db} = 0.6 \epsilon$ in the main plot and $\sigma_g = 0.6 \sigma^{-2}$ in the inset.

motion of the droplet and lead to a successful durotaxis case. Still, the inset of Fig. 6b reflects the observed behavior caused by an average ‘force’ that propels the droplet. Finally, we have clearly seen from our data that unsuccessful durotaxis cases are characterised by a flat interfacial energy that fluctuates around a constant value, which would ideally yield $f_x \approx 0$.

To further understand the durotaxis mechanism of droplets on brush substrates, we have gone one step further and tried to identify the origin of the changing interfacial energy in successful durotaxis cases. In particular, we have measured the standard deviation of the end-to-end distance, Ω , which describes the width of the free-end positions distribution of the brush polymer chains (Fig. 7a), i.e., the surface roughness of the brush. We can observe that Ω decays monotonically towards the stiffest parts of the brush. In other words, stiffer polymer chains exhibit a smaller extent of fluctuations concerning the end-to-end distance of the polymer chains, which is generally expected when the stiffness increases. Moreover, we

can see that the decay of Ω is faster at the soft parts of the substrate and generally follows the decay in the interfacial energy (Fig. 6). The inset of Fig. 7a presents results for the density profile in the z direction at different positions X in the x direction (along the stiffness gradient). We observe that the thickness of the brush surface becomes smaller towards the stiffer parts, which would correspond to a flatter surface locally. In contrast, slower decaying density profiles correspond to a larger thickness of the brush surface, in other words, to a rougher brush surface, which is observed in the soft substrate parts. In practice, rough surfaces result in a smaller number of contacts with the droplet, and as a result a higher (less negative) interfacial energy.¹³ On the contrary, a flat profile would allow for a larger number of contacts between the droplet and the substrate. For this reason, the droplet moves towards the stiffer parts of the substrate. We provide further evidence for our argument by measuring the interpenetration length, W , as a function of the position, X , of the centre-of-mass of the droplet along the substrate in the direction of the stiffness gradient (Fig. 7b). This property reflects the average distance of the substrate–droplet contact pairs, which is noted here with the symbol l_z . We can clearly see that the interpenetration length decreases at the stiffer parts of the substrate, which points to a sharper (flatter) brush surface, in accordance with the results of Fig. 7a. We have further explored the dependence of W on ε_{db} and σ_g and found that it decreases as a function of σ_g due to the induced stiffness by the steric interactions between the brush polymer chains, while it increases with ε_{db} . An important conclusion from the results of Fig. 7c is that W is clearly larger in the case of soft brushes ($k_\theta = 0 \text{ } \epsilon/\text{rad}^2$). However, it is the gradual change of this roughness that plays an important role in inducing the interfacial gradient, which in turn translates into the effective ‘force’ that drives the droplet motion.

With these indications that the minimization of the interfacial energy drives the droplet toward areas of more negative energy, in Fig. 8, we show the interfacial energy for the same systems shown in Fig. 5. When the chain length of the droplet polymer chains, N_d , varies within the range considered in our study, there are no noticeable changes in the interfacial

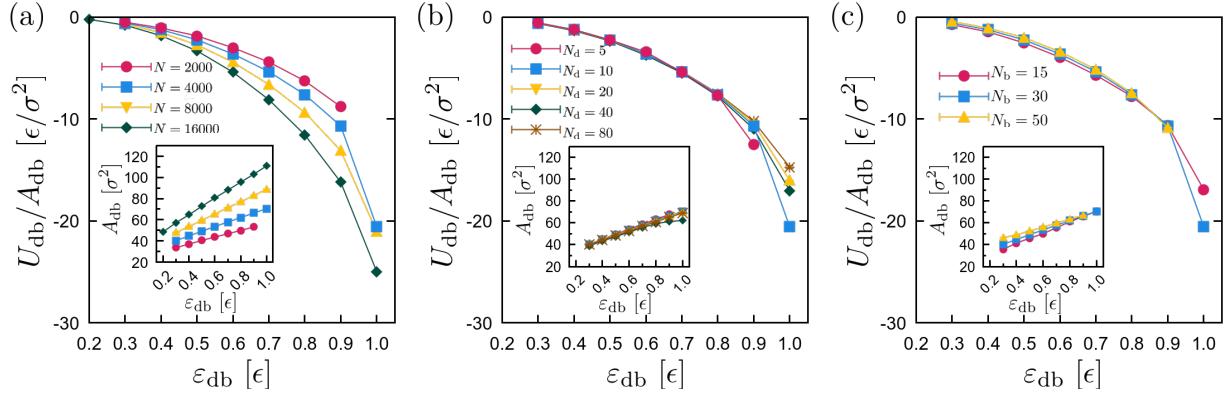


Figure 8: Droplet–brush interfacial energy, U_{db} , per area of the droplet–substrate contact surface, A_{db} , as a function of ε_{db} . $\sigma_g = 0.6 \sigma^{-2}$ and $\Gamma = 0.8 \epsilon/\text{rad}^2\sigma$. Panels show results for different (a) N ($N_b = 30$ and $N_d = 10$ beads), (b) N_d ($N_b = 30$ beads), and (c) N_b ($N_d = 10$ beads). The area, A_{db} , was calculated by using the qhull library,⁶⁴ taking the area of the convex hull.

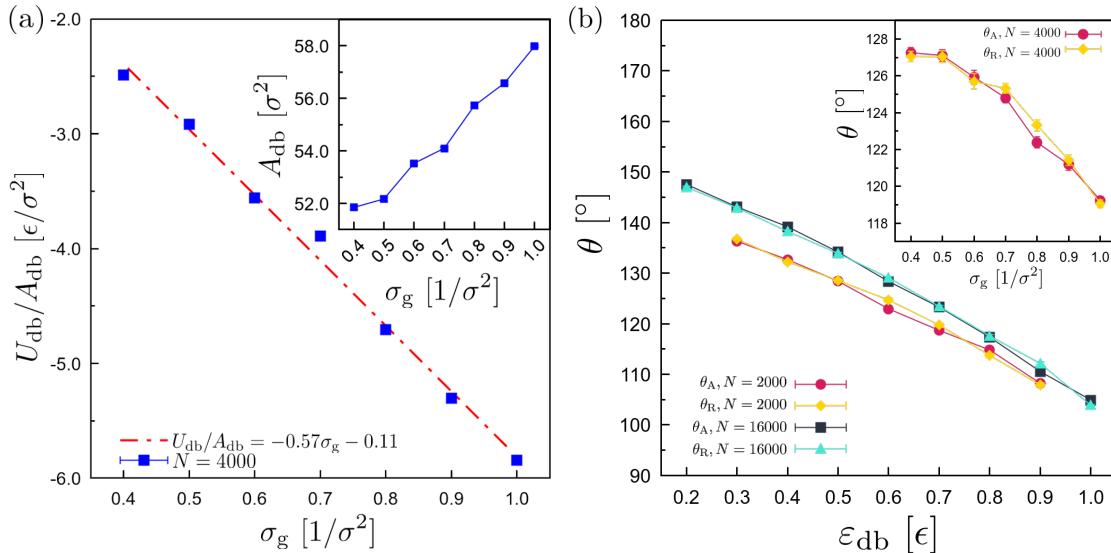


Figure 9: (a) Droplet–brush average interfacial energy, U_{db} , per area, A_{db} , as a function of the grafting density, σ_g . Dashed-dotted line is the result of a linear fit with slope -0.57ϵ as indicated. Inset illustrates the values of the area, A_{db} , versus the grafting density. $\varepsilon_{\text{db}} = 0.6 \epsilon$, $N = 4000$, $N_b = 30$ and $N_d = 10$ beads. $\Gamma = 0.8 \epsilon/\text{rad}^2\sigma$. (b) Advancing, θ_A , and receding, θ_R , contact angles along the durotaxis motion (x direction) as a function of ε_{db} for droplets of different size as indicated. $\sigma_g = 0.6 \sigma^{-2}$. The inset shows the dependence of the contact angles on the grafting density, σ_g , for $\varepsilon_{\text{db}} = 0.6 \epsilon$. In both the main panel and the inset, $N_d = 10$ and $N_b = 30$ beads, and $\Gamma = 0.8 \epsilon/\text{rad}^2\sigma$.

energy (Fig. 8b) and systems are rather characterised by an equivalent average energy profile, which is reflected in the average velocity of the droplets (Fig. 5b). There, we have found that

a change in the viscosity of the droplet does not significantly affect the durotaxis efficiency. Slight changes in the average interfacial energy are observed when the brush chain length, N_b , varies (Fig. 8c). These results are also consistent with those of Fig. 5c. In particular, we can see that the brush with chain length $N_b = 50$ beads appears to have the lowest average interfacial energy and the largest interfacial area for the whole range of ε_{db} considered here. Moreover, differences in the interfacial energy between the systems with different N_b become smaller as ε_{db} increases, which is much clearer in the data concerning the interfacial area, A_{db} , in line with the results of Fig. 5c. In contrast, rather larger differences are observed when the size of the droplets, N , changes (Fig. 8a). In particular, droplets of smaller size have a markedly lower (less negative) interfacial energy per area than larger droplets. These differences become more apparent as the strength of interactions, ε_{db} , increases. Interestingly, although the energy here shows a monotonic behavior, this is not the case for the average velocity of the droplet (Fig. 5a), which indicates that droplets of different size are differently affected in a global sense for a given set of substrate parameters. One contributing factor is that the change in interfacial energy from soft to hard substrate is proportional to the contact area $\propto N^{2/3}$, while the mass is proportional to N . Therefore the energy change per atom is $\propto N^{-1/3}$, other factors being equal, and the velocity change can be expected to scale as $N^{-1/6}$. This is not inconsistent with Fig. 5a at medium strength ε_{db} . Finally, the interfacial energy decreases proportionally to the grafting density, with a slope of -0.57ϵ (Fig. 9a), suggesting a proportionally larger number of contacts between the droplet and the substrate as the grafting density grows.

We have also monitored the advancing, θ_A , and receding, θ_R , contact angles during the durotaxial motion and results are presented in Fig. 9b for typical cases. In this case, the angles have been determined by using the curvature of the droplet as described in previous studies,⁶⁵ thus avoiding error-prone fits. We observe that both θ_A and θ_R decrease rather linearly with the increase of ε_{db} . A linear decrease has been observed for droplets on solid substrates.^{13,65} Droplets of different size, namely $N = 2000$ and $N = 16000$ beads show the

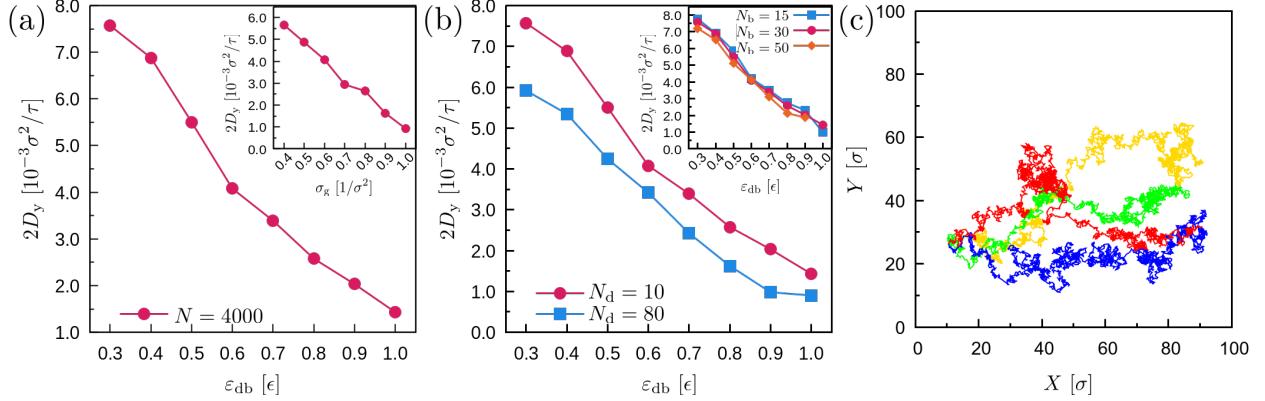


Figure 10: Diffusion coefficient ($\sigma_g = 0.6 \sigma^{-2}$) as a function of (a) ε_{db} (the inset shows the dependence on the grafting density, σ_g for the case $\varepsilon_{\text{db}} = 0.6 \epsilon$). $N_d = 10$ and $N_b = 30$ beads. (b) Diffusion coefficient for different droplet chain length, N_d , brush chain length, N_b (inset) as a function of ε_{db} . $\sigma_g = 0.6 \sigma^{-2}$, $\varepsilon_{\text{db}} = 0.6 \epsilon$ in the inset. $N = 4000$ beads. (c) Typical, successful durotaxis trajectories of the centre of mass of the droplet in the $x - y$ space as indicated by different colours for separate run. $\sigma_g = 0.6 \sigma^{-2}$, $\varepsilon_{\text{db}} = 0.6 \epsilon$, $N = 4000$, $N_b = 30$ and $N_d = 10$ beads, and $\Gamma = 0.8 \epsilon/\text{rad}^2\sigma$.

same trend. Moreover, as ε_{db} increases, the differences between smaller and larger droplets become less pronounced. A much weaker dependence of the contact angles on the grafting density has been observed for $\sigma_g \leq 0.6 \sigma^{-2}$ and a small scale rather linear dependence for $\sigma_g \geq 0.6 \sigma^{-2}$. Our results, which are averaged over the whole trajectory, do not show any statistically significant difference between advancing and receding contact angles. Due to the greater magnitude of interfacial energy (more negative) at the stiffer parts of the substrate (Fig. 6) one would expect a smaller advancing contact angle (for example, as Fig. 9b suggests, larger attraction leads to smaller contact angles). Slightly larger values for the receding contact angle, θ_R , are observed consistently for different values of σ_g and ε_{db} , but, still, within the statistical error. In experiment and theory, when the droplet moves by steadily applied external force the receding contact angles are smaller than the advancing ones in which case friction effects might also play a role.

Finally, to investigate the diffusion of the droplet, and how it is affected by the main parameters, we have analysed the movement of the centre of mass of the droplet in the y direction (Fig. 10). Dynamics in the y direction is free of extraneous effects due to grafting

density gradient and the durotaxis itself, so serves as a good control and measurement of the diffusion properties. Overall droplets with higher viscosity and larger wettability on the brush substrate, show a slower diffusion. The same effect has the grafting density. In contrast, N_b does not have a tangible effect on the droplet motion. In Fig. 10c, we present typical trajectories as a function of the X and Y positions of the droplet centre-of-mass. We can observe that durotaxis motion is also characterised by significant random motion in both x and y axes including ‘reversals’. In some cases, we can observe that the droplet can cover in the y direction a distance as much as 30% of the total distance in the x direction, which suggests that durotaxis motion is also strongly affected by random effects at the interface between the droplet and the substrate, especially when the gradient of the interfacial energy becomes small, *i.e.*, the driving force of the durotaxis is correspondingly small.

CONCLUSIONS

In this study, we have proposed a new design of brush polymer substrates that is capable of leading to the durotaxis motion of nanodroplets. The knowledge gained here may lead to new experimental brush-based substrate designs and provide further understanding of relevant biological processes, such as the motion of cells on tissues,^{11,12} or the mucus flow around lung cilia.⁵⁵ Our analysis has also indicated that the durotaxis motion on brush substrates is driven by a corresponding gradient in the interfacial energy between the droplet and the substrate, in line with previous findings in the context of various other substrate designs.^{13,16,24} Moreover, we have found that the origin of the steady increase of the interfacial energy is related to the state of the brush surface, which appears as a ‘rougher’ profile in the softer parts of the substrate and a flatter interface in the stiffer regions. This translates into a larger number of contacts between the droplet and the substrate in the stiffer parts, and hence a more negative interfacial energy along the direction of the stiffness gradient.

We have also conducted a parametric study based on the various system parameters in

order to gain further insight into the system and identify the key parameters of the brush substrate design. Two of the key parameters are the grafting density of the polymer chains and the substrate wettability. Our findings suggest that the durotaxis motion is favored by a moderate grafting density, which in our case translates to values of grafting density $\sigma_g \approx 0.5 \sigma^{-2}$, and the same time moderate values of the substrate wettability, namely $0.5 \epsilon \leq \varepsilon_{db} \leq 0.9 \epsilon$. Surprisingly, we have found that the stiffness gradient itself, as defined by the linear change in the stiffness of individual polymer chains tuned by the harmonic constant, k_θ , does not induce important changes in the efficiency of the durotaxis motion. This might be due to the relatively large grafting density, which affects the apparent stiffness of the polymer chains, thus minimising the actual effect of the gradient. Such an effect has not been observed in previous systems.¹³ Moreover, the droplet viscosity also seems not to affect the durotaxis efficiency as also the length of the polymer brush chains, since the durotaxis performance seems to saturate after a certain polymer length. In contrast, the size of the droplet plays a role. In particular, smaller droplets seem to reach a faster durotaxis and for a lower adhesion to the substrate, while larger droplets move with a lower average velocity exhibiting their maximum velocity at larger droplet–substrate adhesion. Furthermore, we have not identified any tangible differences between the advancing and receding contact angles during the durotaxis motion. The durotaxis motion is induced by tiny effects at the droplet–substrate interface as judged by the gradient in the droplet–substrate interfacial energy. Hence, there is a back and forth wiggling motion while the brush slowly guides the droplet towards a lower energy state. Finally, we have discussed how our findings could motivate further experimental research in the area of self-sustained fluid motion on brush gradient substrates. It would also be interesting to investigate the droplet durotaxis behavior when many droplets are placed onto the substrate and explore various effects, such as droplet coalescence or how the droplet–substrate interactions are affected in populations of droplets. Further work to explore such possibilities is expected in this direction in the future. We anticipate that this study for the first time presents

new possibilities for the implementation and understanding of durotaxis motion of fluids on brush substrates with important implications for various areas, for example, in the context of biology.

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Supporting Information Available

M*.mp4: Movie illustrates an example of durotaxis motion onto a gradient brush substrate. The parameters for the system are: $N = 4000$, $N_d = 10$, and $N_b = 30$ beads. $\sigma_g = 0.6 \sigma^{-2}$, $\Gamma = 0.8 \epsilon/\text{rad}^2\sigma$ (chains at the very soft right end are fully flexible, *i.e.*, $k_\theta = 0 \epsilon/\text{rad}^2$, while at the very stiff part $k_\theta = 80 \epsilon/\text{rad}^2$), and $\varepsilon_{db} = 0.6 \epsilon$.

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Graphical TOC Entry

