Analysis of the kinetic behavior of chains and clusters

Experimental observation of beads and clusters

For efficient Ag capture from an analyte solution flow, a magnetic particle plug extending across the microchannel needs to be generated. Thus, interaction between beads in the presence of a magnetic field, in particular the formation of chains and clusters, has to be considered for a realistic description of the system. In the following, we analyze how this affects the characteristic parameters and performance of the system compared to the previously described behavior of single particles.[1] As illustrated in the image sequence in Fig. S1a, there is experimental evidence that the velocity increases with the number of aggregated particles. The photographs show a single bead, bead chains with different lengths and clusters moving across the microchannel in the presence of a magnetic field. The relative distance of aggregates with different size increases in time, indicating their velocity difference. These aggregates are schematically displayed in Fig. S1b-d. Chains and clusters are oriented in parallel to the magnetic field lines. We determined experimentally the mean velocity of different aggregates by analyzing image sequences taken with a fast video camera (Pixelink PL-B741U, Ottawa, USA). Quantitative data of the velocity for single-stranded chains comprising up to 17 beads are reported in Fig. S2. In our system, the speed of a single bead crossing the microchannel is typically 0.4±0.1 mm/s, whereas a doublet travels with a speed in the range of 0.8±0.1 mm/s. Larger chains may move up to 3 times faster than single beads.

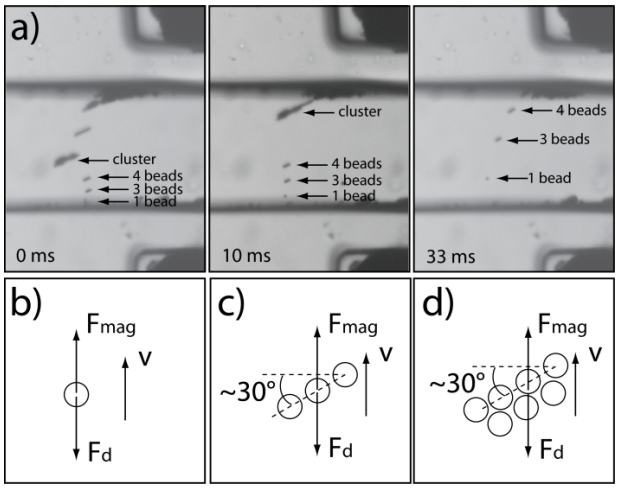

Fig. S1 a) Sequence of photographs (time lapse 33 ms) taken with a high speed camera showing bead aggregates of different size crossing the microchannel in the presence of a magnetic field. An increasing distance in time indicates a higher velocity of the larger aggregates. Three configurations are considered for theoretical analysis: b) a single bead, c) a single stranded chain and d) a cylindrical cluster. F_{mag} and F_d are the magnetic and the viscous drag force, respectively.

Theoretical models for chain and cluster motion

In literature, the magnitude of the magnetic force F_{mag} and the viscous drag force F_d are generally considered for a single particle.[1, 2] In steady state conditions, both forces are equal and the equilibrium velocity of a single bead can be derived. The particular dynamic behavior of chains or clusters in a viscous medium under the presence of a magnetic field is often not taken into account. It was shown previously that the velocity of a chain increases with the number of magnetic particles for motion parallel to its axis.[3, 4] Sedimentation of magnetic clusters with a relatively large number of beads was also discussed for motion parallel or perpendicular to the symmetry axis.[5, 6] With the dynamic plug configuration in the present device, motion perpendicular to the chain axis is of particular interest.

We consider the fluidic resistance of a cylindrical object as a general model for chains and larger clusters. An approximation for the drag force on a cylinder moving perpendicular to its axis was given as [3, 7]

$$F_{d,cylinder} \approx \frac{C_1 \pi \eta v a}{\ln\left(\frac{2a}{b}\right) + C_2} \tag{S1}$$

where a is the length and b the radius of the cylinder, η is the viscosity of the medium and v is the velocity of the particle. It was pointed out by Derks *et al.* that the dimensionless constants C_1 and C_2 in eqn (S1) depend on the experimental conditions.[3]
Assuming that the magnetic force exerted on a chain of beads is directly proportional to the number of beads,

$$F_{mag,chain} = nF_{mag,bead} \tag{S2}$$

where n is the number of beads in a chain (with $a = 2rn$, r is the bead radius) and equalizing this force to the viscous drag force of eqn S1, results in the logarithmic dependence given by equation S3.

$$v = A\ln(n) + B \tag{S3}$$

The fit of the experimental data based on eqn (S3) is shown in Fig. S2 (with A = 0.36 and B = 0.43). The quality of this fit is satisfactory (χ^2_{red}=0.93 and R^2=0.91). A similar behavior was found by Derks *et al*. for chains moving parallel to the axis in a dedicated mm-sized magnetic bead manipulator with a static magnetic field configuration.[3] Our findings show that this logarithmic law also holds for motion perpendicular to the symmetry axis and on the scale of a microchannel.
Analytical approximations for the viscous drag force for chains of 2, 3 and 4 beads have been derived by Burgers.[7, 8] These expressions take into account the distortion of the Stokes field around one bead flowing behind another bead. A frictional coefficient λ was introduced that accounts for the fluidic resistance experienced by the chain, i.e. for the increase of the drag force ($F_{d,bead} / F_{d,chain} = \lambda_n$ with $\lambda_n < 1$). As an example, the resistance coefficient for a bead pair is given by[7]

$$\lambda_2 = \frac{1}{2}\left(1 + \frac{r}{l}\right) \tag{S4}$$

where r is the bead radius and l is the distance between the centers of the outer spheres of a chain (valid for small r/l and random chain orientations). Assuming that beads are in close contact (r/l=0.5), due to magnetic attraction for instance, we

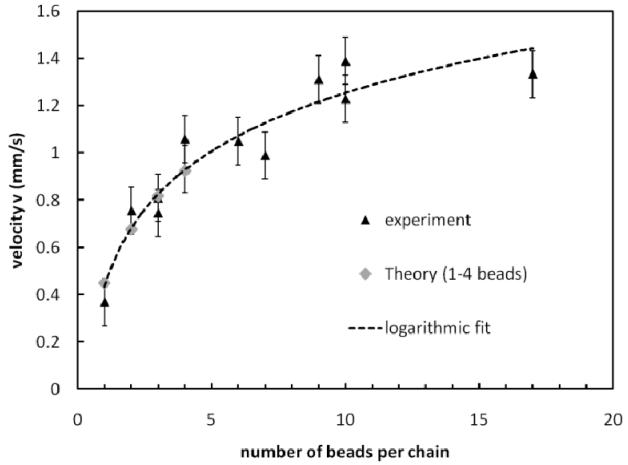

Fig. S2 Velocity of single-stranded chains *vs* number of beads in the chain for motion across the microchannel in the magnetic field. Error bars are related to the pixel resolution of the camera. The fit of the experimental data derived from a cylindrical model for the chains (dashed line) shows a logarithmic increase of the velocity. Calculated values based on an analytical approximation taking into account the real shape of the chains are also indicated (for 1 to 4 beads).

obtain $\lambda_2^{-1} \cong 1.33$. For saturated beads, the magnetic force is proportional to the number of beads, thus a pair of beads is expected to travel 1.5 times faster than a single bead. According to the same model, we obtain $\lambda_3^{-1} \cong 1.65$ and $\lambda_4^{-1} \cong 1.95$ for 3 and 4 beads in close contact, respectively. Chains with four beads are therefore expected to travel two times faster than single beads in a given magnetic field. It is interesting to note that the effective fluidic resistance per bead decreases when their number in the chain increases. Velocity values for 2, 3 and 4 beads have been calculated with this model and are indicated in Fig. S2. We find that the calculated values for small chains correspond well to the logarithmic increase derived for the cylindrical model discussed above. From this result, we conclude that a simplified cylindrical model based on eqn (S1) is a valid approach to describe the kinetics in this type of magnetic bead-based systems using the empirically determined constants C_1=3.8 and C_2=-0.17. These constants differ from the values proposed by Burgers for a cylinder (C_1=8 and C_2=0.5) due to the pearl-like shape of the chains. [7, 9]

For increasing bead concentrations, formation of larger clusters of agglutinated beads and chains becomes more likely. Experimental observation shows that clusters may travel up to 4.0±0.1 mm/s in the magnetic field configuration of our system, i.e. up to 10 times faster than single beads. As an example, we consider a cylindrical approximation of the cluster indicated in Fig. S1d. With an estimated number of about 100 beads (with a = 15 µm and b = 1.5 µm, packing factor 0.5, C_1=8 and C_2=0.5) and by using eqn's (1), (S1) and (S2), we find a theoretical velocity of 3.8 mm/s, which is in good agreement with the measured value.

Taking into account transversal velocities up to several mm/s for different aggregates sizes, we have chosen a frequency of 70 Hz for the AC field. This frequency is high enough to maintain most of the beads, chains and even clusters in continuous motion across the microchannel, thus avoiding temporary immobilization on the side walls.

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