Abstract

Particles that can be trapped in optical tweezers range from tens of microns down to tens of nanometres in size. Interestingly, this size range includes large macromolecules. We show experimentally, in agreement with theoretical expectations, that optical tweezers can be used to manipulate single molecules of polyethylene oxide suspended in water. The trapped molecules accumulate without aggregating, so this provides optical control of the concentration of macromolecules in solution. Apart from possible applications such as the micromanipulation of nanoparticles, nanoassembly, microchemistry, and the study of biological macromolecules, our results also provide insight into the thermodynamics of optical tweezers.

Introduction—the Limits of Optical Trapping

While optical tweezers (Ashkin et al. 1986) are usually used for the trapping and manipulation of particles of approximately 1–10 µm in size, both larger and smaller particles can be trapped. Since an upper limit to the force that can be exerted by the beam is imposed by the finite momentum flux of the beam, while weight, viscous drag, and the likelihood of adhesion all continue to increase with increasing size, optical tweezers will become unable to perform useful manipulation for sufficiently large particles.

For small particles, the gradient force becomes proportional to the volume, while the scattering forces become proportional to the volume squared (Svoboda and Block 1994; Harada and Asakura 1996). Therefore, a wider range of particles become trappable at small sizes, such as reflective particles that are pushed out of the trap at larger sizes. Absorptive particles remain untrappable at small sizes since the absorption force is proportional to the volume.

The lower limit is provided by Brownian motion—the Brownian motion force is $12\pi \eta k_B T$ where $\eta$ is the viscosity of the fluid and $k_B$ is Boltzmann’s constant. Since the viscosity of the fluid will hinder escape, it is best to compare the trapping potential—the energy required to remove the particle from the trap—with the thermal energy $k_B T$. 

Nanotrapping and the thermodynamics of optical tweezers

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Since the gradient force acting on a small sphere is given by (Harada and Asakura 1996)

$$F_{\text{grad}} = \frac{2\pi n_{\text{med}} a^3}{c} \left( \frac{m^2 - 1}{m^2 + 2} \right) \nabla I$$  \hspace{1cm} (1)

where $n_{\text{med}}$ is the refractive index of the surrounding medium, $m = n_{\text{particle}}/n_{\text{med}}$ is the relative refractive index, $c$ is the speed of light in free space, and $I$ is the irradiance $I$, the corresponding trapping potential is equal to

$$U = \frac{\pi n_{\text{med}} a^3}{c} \left( \frac{m^2 - 1}{m^2 + 2} \right) I.$$  \hspace{1cm} (2)

This suggests that it should be possible to trap polymer microspheres as small as 30 nm in radius with a power as low as 100 mW available at the focus. As this size range includes single polymer macromolecules, we carried out experiments on the optical trapping of single polyethylene oxide (PEO) molecules of differing molecular weights (Singer et al. 2006).

**Experiment and Experimental Results**

A typical inverted optical tweezers apparatus, with a $100 \times \text{NA} = 1.25$ objective, was used to focus the beam from a 1064 nm ytterbium fiber laser to form the trap. Up to 700 mW was available at the focus. A sample consisting of a suspension of PEO molecules was placed in the trap, and the concentration of PEO molecules in the trap was monitored by measuring the backscattered light from a low-power (2 mW) He–Ne laser focused onto the same position. The properties of the PEO molecules are given in tables 1 and 2. Notably, a comparison of measured radii of gyration (Devanand and Selser 1991) with the stretched chain lengths (Cooper et al. 1991) shows that the PEO molecules can be approximated as spheres, and that the above theoretical considerations should apply.

**Table 1. Concentrations of PEO solutions**

| molecular weight (kDa) | number density ((µm)$^{-3}$) | mass fraction | concentration:overlap |
|------------------------|-------------------------------|---------------|----------------------|
| 100                    | 313                           | 0.01%         | 0.02                 |
| 300                    | 281                           | 0.027%        | 0.07                 |
| 900                    | 268                           | 0.077%        | 0.48                 |

**Table 2. Radii of gyration and stretched chain lengths of PEO molecules**

| molecular weight (kDa) | radius of gyration (nm) (Devanand and Selser 1991) | stretched chain length (µm) (Cooper et al. 1991) |
|------------------------|------------------------------------------------------|-------------------------------------------------|
| 100                    | 17.6                                                 | --                                              |
| 300                    | 33.5                                                 | 2.4                                             |
| 900                    | 63.6                                                 | 7.2                                             |

The two larger sizes of PEO molecules (100 kDa and 300 kDa) could be trapped. When the molecules were trapped the concentration of PEO molecules was observed to increase over several minutes. A typical experimental curve is shown below in figure 1.
The increase in concentration was repeatable, reversible, and increased with increasing power (Singer et al. 2006). We estimate that approximately 1.5 W would be required to trap the 100 kDa PEO molecules.

Thermodynamics of Optical Tweezers

The increase in concentration takes several minutes because PEO molecules must diffuse into the region of the trap. As the trap is initially turned on, the molecules around the edge of the trap are rapidly pulled into the middle of the trap. This leaves a region of reduced concentration into which molecules outside the trap will diffuse into.

In the dilute limit, the probability of finding a particle in a particular position will follow a Boltzmann distribution. Since the ambient energy is $k_B T$, and a particle within the trap has its energy reduced by the trapping potential, the probability per unit volume of finding a particle within the trap is greater, and the equilibrium concentration will be

$$C(r) = C_0 \exp\left(-\frac{U(r)}{k_B T}\right),$$

where $C_0$ is the ambient concentration and $U$ is the trapping potential. As soon as the laser power is sufficient for the trapping potential to exceed $k_B T$, the concentration increases very rapidly with increasing power. This results in the appearance of sudden switching-on at a threshold power—also seen in other systems, such as, for example, diodes in circuits, which have similar exponential behaviour.

At equilibrium, there are two opposing forces acting on the molecules: the optical gradient force, and a force due to the gradient of the partial pressure of the molecules. At equilibrium,

$$F_{\text{grad}} C = RT \nabla C$$

where $R$ is the universal gas constant (Einstein 1905; Einstein 1956). Before equilibrium is reached, the imbalance between these two forces will drive diffusion of the PEO molecules. Assuming spherical sym-
metry of the trap, this reduces to a one-dimensional differential equation and can be solved using a finite-difference time-domain method. As the timescales involved—the time over which the optical force moves the molecules, and the time taken to diffuse into the region of the trap—are very different, the simulation requires a very large number of time steps to show the behaviour seen in the experiments. The simulation was carried out with a weak optical force to reduce the discrepancy between the two time scales. Results are shown in figures 2 and 3.

Figure 2. Change in concentration over time. (a) shows the growth of the maximum concentration over time, (b) shows the change in the minimum concentration over time. (c) shows the times at which the concentration profiles shown in figure 3 occur.

Figure 3. Concentration over the trap at different times

In figure 2(a), we can see the growth in concentration over time. This is similar to the experimentally observed behaviour in figure 1. The depletion of concentration in the outer region of the trap is shown
Although we could not directly observe this depletion, it clearly existed in the experiment, since otherwise PEO molecules would not have diffused towards the trap. The rapidity of the initial depletion compared with the slow increase back to the ambient concentration highlights the difference in the time scales of the two processes. In order to see how the concentration changes in more detail, the concentration was plotted as a function of position for selected times, shown by the light blue lines in figure 2(c). (Figure 2(c) is otherwise the same as figure 2(b), except with a logarithmic scale on the horizontal axis.) The plots of the concentration versus position are shown in figure 3. The dark blue line shows the instantaneous concentration, with the light blue line indicating the initial concentration. The magenta line shows the profile of the trapping beam, which is assumed to be Gaussian. The initial depletion due to the optical trap concentrating the immediately available molecules in the centre of the trap can be clearly seen, followed by a slow approach to equilibrium.

Interestingly, the edge of the optical trap functions as a one-way barrier for the molecules—they can diffuse into the trap, but until the partial pressure of the molecules already in the trap is sufficiently high, they cannot diffuse out. The surface area of this “event horizon” through which the molecules fall increases with increasing power, which is why the rate of increase of concentration was observed to increase in the experiments (Singer et al. 2006).

**Conclusion**

We have shown that optical tweezers can be used to control the concentration of macromolecules in solution. These results illuminate the thermodynamics of optical tweezers, and provide a striking example of diffusion under an applied force. This suggests that optical tweezers may be a useful tool to study the equilibrium and non-equilibrium thermodynamics of polymer or other molecules in solution.

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