입자추적 미세유변학의 묽은 점탄성 물질에 대한 응용

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Particle Tracking Microrheology and its application to dilute viscoelastic materials.

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Abstracts

Soft materials, such as polymer solutions, gels and filamentous protein materials in cells, show complicated behavior due to their complex structures and dynamics with multiple characteristic time and length scales. Several complementary techniques have been developed to measure viscoelastic properties of soft materials. Especially, particle tracking microrheology, using the Brownian motion of particles in a medium to get rheological properties, has recently been improved both theoretically and experimentally. Compared to other conventional methods, video particle tracking microrheology has some advantages such as small sample volume, detecting spatial variation of local rheological properties, and less damage to sample materials. With these advantages, microrheology is more suitable to measure the properties of complex materials than other mechanical rheometries.

Theory

When a particle is immersed in a viscoelastic fluid, its motion can be described by the so called generalized Langevin equation.

$$m\frac{dv(t)}{dt} = f_R(t) - \int_0^t \zeta(t-t')v(t')dt'$$

where $f_R(t)$ represents all the forces acting on the particle, including both the inter-particle forces and stochastic Brownian forces.

By taking the unilateral Laplace transform to treat the convolution integral term in the above equation and neglecting inertia, we can get the viscoelastic memory function related to the velocity autocorrelation function

$$\tilde{\zeta}(s) = \frac{k_B T}{\langle v(0)\tilde{v}(s)\rangle} = \frac{6k_B T}{s^2\langle \Delta\tilde{r}^2(s)\rangle}$$

In the laplace domain, using the Stokes law, we can relate microscopic memory function to the bulk viscoelasticity.

$$\tilde{G}(s)=\frac{s\tilde{\zeta}(s)}{6\pi a}$$

By combining above two equations, we can relate the mean square displacement of the probe particle to the bulk relaxation modulus in the Laplace space.

$$\tilde{G}(s)=s\tilde{G}_r(s)=\frac{k_B T}{\pi a s\left\langle \Delta\tilde{r}^2(s)\right\rangle}$$

This equation is called generalized Stokes-Einstein equation, and by using this equation we can get viscoelastic responses of material from observed mean square displacement of probe particles. Therefore, If we get the mean square displacement of probe particles and apply unilateral Laplace transformation to that data, we can acquire relaxation modulus and thus other viscoelastic properties of sample material from above equation.

Experiments

1μm diameter carboxylate-modified fluorescent probe particles (Molecular Probe, US) were used so that their surface chemistry was compatible to the sample.

Samples were observed in a Olympus inverted epifluorescence microscope with 60X oil-immersion objective lens (Olympus, Japan, N.A. 1.3.). Samples were treated and sealed carefully to prevent convectional flows and evaporations which can cause serious errors in this experiment. The mean square displacements of the probe particles were captured using a 1000X1000 pixels EM-CCD Camera (Hamamatsu, Japan) and PC-Camlink Capture Board (Coreco, Canada). Frames were captured about 100s and their rate were 30 frames/s. To reduce the inter-particle interactions, particles that were less than 10 particle-diameters apart form neighboring particles were excluded.

Sequence of images were captured with HIPic software (Hamamatsu, Japan) and probe particles were tracked using IDL based multiple particle tracking code that has been developed by Crocker and Grier with some our modifications.

Results and Discussions

Our Experiments were carried out for two kinds of samples. Firstly, Newtonian viscosity of water was obtained to certify our experimental set-ups and modified particle tracking code.

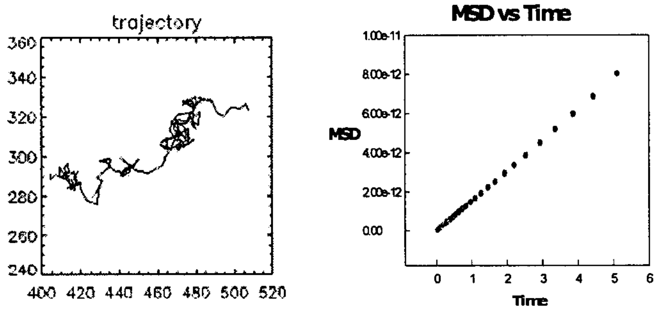
It is well known that for the Newtonian fluid, the mean square displacements of the probe particles are directly proportional to the diffusivity and time.

$$<r^2> = 4Dt$$

Using the diffusivity obtained from above equation, we calculated viscosity of water by following equations

$$\eta = \frac{k_B T}{6\pi a D}$$

Typical particle tracking results are as followed.

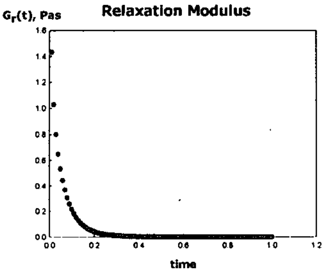


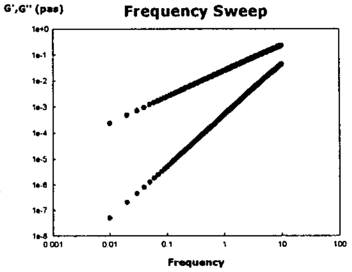
(a) (b)

<Fig. 1 Typical particle trajectory results. (a) particle trajectory of single particle. (b) time versus mean square displacement data

Fig. 1 (a) represents single probe particle trajectory. Both x and y coordinate represents pixels in a image which is equivalent to moving distances. Because we used 60X objective lens and 8mmX8mm CCD camera, each pixel is about 133 nm. Fig. 1 (b) represents ensenble averaged mean square displacements of many particles and all dimensions are in SI units. From Fig. 1 (b) data we can get an diffusivity of probe particle immersed in water and from that we calculated viscosity of water as 1.075 (cp). To verify this results, we compared this to the ARES experimental results and we have a nice agreement with that conventional rheometer which predicts viscosity of water as 1.017 (cp).

Secondly we applied this method to the viscoelastic materials. In this time, contrary to the above case, we must use generalized Stokes-Einstein equation shown in the theory part to get relaxation modulus and the dynamic data of the sample. Sample used in this experiment is commercially available colloidal silica solution LUDOX (DuPont, US) and the results are shown as followed.





Due to the lack of inertia effect, we can get low frequency data of low viscosity material and thus, we expect, this method can be applied to study the micro-structure of low viscosity materials such as fumed silica or block copolymer solutions.

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References

1. T. G. Mason et al., J. Mol. Structure, 383, 81 (1996)
2. T. G. Mason et al., J. Opt. Soc. Am. A. 14, 139 (1996)
3. A. J. Levin et al., Physical Review Letters, 85, 1774 (2000)
4. Waigh. T. A. , Reports on Progress in Physics, 68, 685 (2005)
5. J. Apgar et al., Biophysical Journal, 79, 1095 (2000)
6. F.C. MacKintosh et al., Current Opinion in Colloid & Interface Science, 4, 300 (1999)
7. V. Breedveld et al., J. of Materials Science, 38, 4461(2003)
8. M. J. Solomon et al., Current Opinion in Colloid & Interface Science, 6, 430 (2001)
9. J. C. Crocker et al., Physical Review Letters, 73, 352 (1994)