ICFP – Soft Matter

Microrheology

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Microrheology uses the observation of the thermal motion of a probe particle to measure the viscoelastic properties of the surrounding medium [1]. It allows to do rheology measurements in a non-invasive way and is particularly useful when only small samples of the medium are available, which is the case for instance for the interior of a cell.

A Newtonian fluid is characterised by its viscosity η. The friction coefficient of a spherical particle with radius a in such fluid is $\zeta = 6\pi\eta a$. The velocity $v(t)$ of a colloid with mass m in one direction follows the Langevin equation

$$m\dot{v}(t) = -\zeta v(t) + \eta(t), \tag{1}$$

where the random force $\eta(t)$ is assumed to be a Gaussian white noise, the amplitude of which is set by the Einstein relation: its correlation is $\langle \eta(t)\eta(t')\rangle = 2\zeta T\delta(t-t')$, where T is the thermal energy.

Viscoelastic fluids are characterized by a complex modulus $\tilde{G}(\omega)$, which relates the shear stress $\tilde{\sigma}(\omega)$ to the imposed strain $\tilde{\gamma}(\omega)$ at a pulsation ω: $\tilde{\sigma}(\omega) = \tilde{G}(\omega)\tilde{\gamma}(\omega)$. For a solid, $\tilde{G}(\omega) = E$, the Young's modulus. For a Newtonian liquid, $\tilde{G}(\omega) = i\eta\omega$. For a general viscoelastic fluid, we define its complex viscosity as $\tilde{\eta}(\omega) = \tilde{G}(\omega)/(i\omega)$ and its complex friction coefficient as $\tilde{\zeta}(\omega) = 6\pi\tilde{\eta}(\omega)a$. The time-dependent friction coefficient $\zeta(t)$ is called the "memory function"; it enters the Langevin equation as

$$m\dot{v}(t) = -\int_{-\infty}^{t} \zeta(t-t')v(t')\mathrm{d}t' + \eta(t), \tag{2}$$

where the random force $\eta(t)$ is still assumed to be Gaussian, but its correlations need to be determined. Causality imposes that $\zeta(t) = 0$ for $t < 0$.

Here we compute the correlation function of the velocity, $C(t) = \langle v(t)v(0)\rangle$ and determine the correlations of the random noise. The correlation function depends on the memory function $\zeta(t)$, and thus on the complex modulus in the material.

Technical note: questions requiring calculations are indicated with asterisks: no asterisk for less than three lines of calculations, one for less than 10 lines, and two for longer calculations.

1 Velocity correlations in Laplace space

We look at the process from $t = 0$; the equation (2) becomes

$$m\dot{v}(t) = -\int_{0}^{t} \zeta(t-t')v(t')\mathrm{d}t' + \eta(t). \tag{3}$$

We consider the initial velocity $v(0) = v_0$, as a random value, and assume it to be independent from the noise $\eta(t)$ at times $t > 0$ [2].

1. At equilibrium, how should v_0 be distributed?

2. * Laplace transform the generalized Langevin equation (3), using

$$\hat{v}(s) = \int_{0}^{\infty} v(t)\mathrm{e}^{-st}\mathrm{d}t. \tag{4}$$

Express $\hat{v}(s)$ as a function of the Laplace transform of the memory function, $\hat{\zeta}(s)$, and the noise, $\hat{\eta}(s)$.

3. Determine the Laplace transform of the correlation, $\hat{C}(s)$.

4. Write the Laplace transform of the modulus of the material, $\hat{G}(s)$, as a function of $\hat{C}(s)$.

2 Stationarity condition and correlation function of the noise

We have obtained the desired relation between the velocity correlations and the memory function. However, we have not shown that our assumption of decoupling between v_0 and $\eta(t)$ is consistent, and we have not obtained the correlation of the noise, $N(t) = \langle \eta(t)\eta(0) \rangle$. To show that our assumption is consistent, we show that the process is stationary, $\mathcal{C}(t,t') = \langle v(t)v(t') \rangle = C(t-t')$, provided that the correlation of the noise takes some form, that we determine.

5. From the result of question **2**, write the double Laplace transform of the correlation $\mathcal{C}(t,t')$,

$$\hat{\mathcal{C}}(s,s') = \int_0^\infty \mathrm{d}t \int_0^\infty \mathrm{d}t' \mathrm{e}^{-st-s't'} \mathcal{C}(t,t'), \tag{5}$$

using the double Laplace transform of the noise correlation, $\mathcal{N}(t,t') = \langle \eta(t)\eta(t') \rangle$.

6. * Using only the fact that $\mathcal{N}(t,t') = N(t-t')$, express $\hat{\mathcal{N}}(s,s')$ as a function of $\hat{N}(s)$, and use it to simplify the result of the previous question.

7. Note that the result of the previous question also applies to $\hat{\mathcal{C}}(s,s')$, and use it to write $\hat{\mathcal{C}}(s,s')$ using the result of question **3**.

8. * Comparing the expressions of $\hat{\mathcal{C}}(s,s')$ from questions **6** and **7**, determine $\hat{N}(s)$ and $\langle \eta(t)\eta(t') \rangle$ for the process to be stationary. Why is this relation a fluctuation-dissipation relation?

References

[1] T. G. Mason and D. A. Weitz. Optical Measurements of Frequency-Dependent Linear Viscoelastic Moduli of Complex Fluids. *Phys. Rev. Lett.*, 74(7):1250–1253, Feb 1995.

[2] M. Medina-Noyola and J.L. Del Rio-Correa. The fluctuation-dissipation theorem for non-markov processes and their contractions: The role of the stationarity condition. *Physica A: Statistical Mechanics and its Applications*, 146(3):483–505, 1987.