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FROM RHEOLOGY TO MOLECULAR DETAIL - VISCOSITY OF SUSPENSION OF COMPLEX MOLECULES

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Summary The viscosity of solution is intrinsically connected with its composition and the properties of individual particles. For complex macromolecules there often exist coupling between the flow and the state of the molecule. The distribution of particle shapes and movements reacts to the external flow and the flow reacts to this distribution change. This coupling determines the amount of stress induced by the molecules immersed in the fluid that results in change of the viscosity. Using the Rotne-Prager-Yamakawa approximation we show, that given molecular model, one can infer the details of the molecules based on rheology of the solution.

INTRODUCTION

Relation between effective solution viscosity and its composition, in principle, can be calculated from the Stokes equation. All the details of the system in a given time instant come into the solution. They include particles conformation and position but also characteristics of the external flow. Also the coupling of those play an important role due to the hydrodynamic interactions, since the flow affects particles and particles affect flow. Even the change in the strength of the flow change suspension state and the effective viscosity. These dependencies give an insight into the details of the molecules.

KEY IDEA

The effective viscosity η_{eff} is the proportionality coefficient between the stress tensor and the effective strain tensor. These three quantities are coupled and depend on the suspension and flow. The effective viscosity calculated for shear flow is different than for e.g. straining flow. In this report we will restrict to the shear flow even though the presented method is suitable for any kind of linear flow. For the shear flow stress tensor is given by

$$\boldsymbol{\sigma} = 2\eta_{\text{eff}}\mathbf{E}_\infty \quad : \quad \mathbf{E}_\infty = \frac{1}{2}\left(\nabla\mathbf{v}_0 + (\nabla\mathbf{v}_0)^T\right), \tag{1}$$

where $v_0 = (z\dot{\gamma}, 0, 0)$ is the ambient flow and $\mathbf{E}_\infty$ is the symmetric part of the ambient straining field. The stress tensor can be decomposed into the part originating from unperturbed fluid and the particle contribution

$$\boldsymbol{\sigma} = 2\eta_0\mathbf{E}_\infty + \left\langle \sum_i \boldsymbol{\mathcal{S}}_i \right\rangle_{\dot{\gamma}}, \tag{2}$$

where $\boldsymbol{\mathcal{S}}_i$ is the stresslet induced by particle i and $\langle\cdot\rangle_{\dot{\gamma}}$ denotes an average over all possible particle positions and states for a given flow strength $\dot{\gamma}$. The complete set of the components of the particle induced stresslet consists of: stresslet induced sole by the particle presence, stresslet induced by inter and intra particle forces, stresslet induced by torques acting on particles and stresslet induced by the translational and rotational Brownian motion. Some contributions can be neglected in the specific situations e.g. if all particles in the system are torque-free spheres, then the torque components of the stresslet can be neglected. In the shear flow the effective viscosity η_{eff} can be measured with force acting on the vessel walls required to sustain given shear rate. For the system between two parallel plates in xy plane only the $\boldsymbol{\sigma}_{xz}$ component will contribute to the measurements. In the dilute system - with volume fraction $\phi \ll 1$, the effective viscosity can be expressed in terms of intrinsic viscosity $[\eta]$ by the series expansion[1]

$$\eta_{\text{eff}} = \eta_0\left(1 + [\eta]\phi + O\left(\phi^2\right)\right). \tag{3}$$

For the arbitrary shear strength the intrinsic viscosity can be calculated as

$$[\eta] = \circ\,\frac{1}{\dot{\gamma}}\left\langle \sum_i \boldsymbol{\mathcal{S}}_i \right\rangle_{\dot{\gamma}}. \tag{4}$$

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METHOD

The total stresslet induced by every particle is calculated from the mobility matrix $\boldsymbol{\mu}$. Mobility matrix can be calculated for many different systems using bead models in different approximations. Here we use the Rotne-Prager-Yamakawa (RPY) approximation for the mobility matrix. This matrix is positive definite also for overlapping spheres of different radii[2]. Rigid, non-rigid and partially rigid molecules can be constructed in order to model real particle shapes that can interact with forces and torques. Depending on the partcle size, the Brownian or deterministic trajectory can be calculated. Finally the stresslet is averaged over the simulated trajectory. The method performance is demonstrated by the comparison of the different dumbbell intrinsic viscosities calculation in figure 1. The flow strength is expressed with dimensionless Péclet number $\mathrm{Pe} = 6\pi\eta a^3\gamma$.

RESULTS

On the example of Hookean dumbbell we show, that the equilibrium length of the spring can be determined based on the viscosity spectrum. We will consider a dilute suspension $\phi \ll 1$, that in practice is calculated as a single dumbbell in an unbounded fluid. Let the Hookean dumbbell be composed of spheres of radius a and a spring with an equilibrium length l_0 and stiffness k. The typical intrinsic viscosity dependence on the shear rate, for three different equilibrium lengths with fixed k is presented in figure 2. Significant shear thinning in rarefied solution is observed.

The simulation results for different l_0 and k show, that for spring constants bigger than certain threshold, the equilibrium length of the spring can be uniquely determined from the viscosity spectrum. There are two distinct regimes

- overlapping regime $l_0 \leq 2a : [\eta] = (a_1 + b_1 l_0 \ \gamma^{c_1 l_0}$,

- non-overlapping regime $l_0 > 2a : [\eta] = (a_2 + b_2 l_0 \ \gamma^{c_2 l_0}$,

where (a_i, b_i, c_i) are two sets constants independent of spring stiffness, that are calculated numerically.
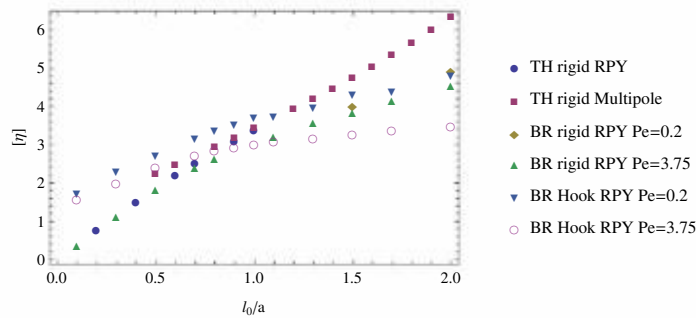

Figure 1: Comparison of intrinsic viscosities: theoretical (TH) results[3] including Brownian contribution for rigid dumbbell (RD) using multipole method and RPY approximation from linear response theory, RD in RPY approximation using Brownian dynamics (BD) and Hookean dumbbell (HD) with $k = 20k_BT$ using BD.
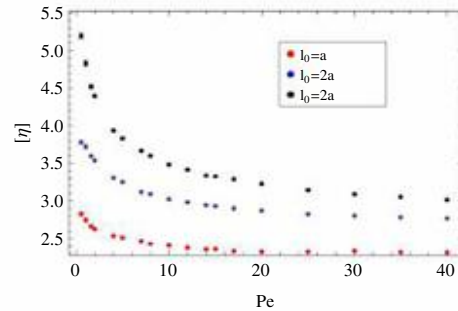

Figure 2: Dependence of intrinsic $[\eta]$ viscosity on the shear rate for $k = 20k_BT$ and different l_0.

CONCLUSIONS

The viscosity of suspension is a result of the coupled interactions between suspension structure and the flow. They both influence each other. Interesting molecular details can be deduced about the shape of the molecules and molecular intractions from the viscosity spectrum by exploiting the knowledge of the hydrodynamic interactions and a proper molecule model. This kind of measurements give insight into molecular details, that are not measurable by other techniques.

References

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