Dilute polymeric solutions close to bounding surfaces:
Shear stresses in equilibrium

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The problem of a dilute polymer solution in equilibrium close to a wall, an edge, and a corner, respectively, is studied theoretically. Detailed knowledge of the rheology in these regions is needed in order to obtain the proper boundary conditions for bulk variables. It is interesting to see that shear stresses are predicted, whose origin is based on the intramolecular (elastic) interaction between the beads.

1 Introduction

In many textbooks on fluid mechanics a fluid is defined as a substance which changes shape when shear stresses are present [1]. This is to be contrasted to the case of a solid in which shear stresses do not initiate a (shearing) motion. Complex fluids, like polymer solutions, suspensions, paints etc. usually exhibit viscous (fluid) and elastic (solid) properties. Thus, the question arises, whether it is possible for viscoelastic liquids not to flow although shear stresses are present. We shall address this problem for one specific example, namely an infinitely dilute polymer solution, modeled as a solution of elastic dumbbells.

In equilibrium this solution is isotropic and shear stresses are absent. This feature is characteristic for the bulk but it need not hold anywhere else, like close to interfaces and walls, respectively. Such regions are atypical [2], since a wall has to be taken care of not only geometrically but also – on the microscale of the particles – hydrodynamically and statistically [3]. For the model studied in this paper only the geometric and the statistical restraints play a role.

Transverse isotropy characterizes the equilibrium situation of one plane wall. Thus, although the direction normal to the wall differs from the two parallel directions, no shear stresses are possible for our fluids with isotropic bulk properties.

Generalizing this idea we expect the symmetry properties of such a fluid in equilibrium to be dictated by the bounding surfaces. This will hold inside
a wall layer, whose thickness is – on dimensional grounds – expected to be of the order of the size of the particles. Though small for many cases of practical interest, the effect can still be rather pronounced. After all only the detailed study of the wall layers will lead to the correct boundary conditions for bulk quantities [4]. An understanding of the physics inside wall layers seems to be called for.

We have chosen to study this problem for a rather simple model fluid, mainly in order to concentrate on the physics of the situation without too complicated mathematics. Hopefully, the understanding gained will lead to theories of more concentrated regimes.

2 Governing equations

For an infinitely dilute solution of dumbbell model macromolecules let \( \Psi(r_1, r_2) \) denote the (bead) distribution function, i.e. probability density of any molecule that bead one is at \( r_1 \) and bead two at \( r_2 \). The beads are assumed to be indistinguishable. The function \( \Psi \) is normalized according to

\[
\int d^3r_1 \int d^3r_2 \Psi = N, \tag{2.1}
\]

where the integration extends over all space accessible to the beads. \( N \) denotes the number of polymer molecules in a given system. Let

\[
R = r_2 - r_1 = (X, Y, Z) \tag{2.2}
\]

denote the relative position between the beads and let \( \phi^c \) denote the intramolecular potential, depending only upon the distance \( R = |R| \) between the beads. Under equilibrium conditions, the use of a Gaussian potential

\[
\phi^c = \frac{1}{2} HR^2 \tag{2.3}
\]

seems appropriate for randomly coiling polymers [5]. The spring constant \( H \) is related to the equilibrium rms legth \( R_{eq} \) via

\[
H = \frac{3kT}{R_{eq}^2}. \tag{2.4}
\]

This being the case, the distribution function in equilibrium will be given by Boltzmann’s law

\[
\Psi_{eq}(r_1, r_2) = n_b \left( \frac{H}{2\pi kT} \right)^{\frac{3}{2}} e^{-\left( \frac{HR^2}{2kT} \right)} \tag{2.5}
\]

with \( n_b \) the polymeric number density in the bulk. Note that Eq. (2.5) requires that no external potentials (like van der Waals, Coulomb, ...) are acting on the polymer, an assumption which we shall use throughout this paper.

The polymeric number density \( n \) will be defined by

\[
n(r) = \int d^3r_2 \Psi(r, r_2). \tag{2.6}
\]