

# The Peclet number for shear thinning in hard sphere dispersions

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## Letter to the editor: The Péclet number for shear thinning in hard sphere dispersions

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The aim of this letter is to introduce an alternative definition for the Péclet number related to the shear thinning of dispersions. We will also demonstrate its significance by using it in the interpretation of published experimental data.

Hard-sphere dispersions show shear thinning due to a transition from a Brownian regime at low shear rates to a hydrodynamic regime at high shear rates. This transition can well be described by the Cross equation (1965) which, if the macroscopic shear rate  $\dot{\gamma}_m$  is written in dimensionless form  $\dot{\gamma}' = \eta_0 \dot{\gamma}_m a^3 / (kT) = \dot{\gamma}_m a^2 / (6\pi D)$ , reads

$$\eta = \eta^\infty + \frac{\eta^0 - \eta^\infty}{1 + (b\dot{\gamma}')^m},$$

where  $\eta$  is the viscosity of the dispersion,  $\eta^0$  and  $\eta^\infty$  are its low and high shear-rate limits;  $\eta_0$  is the liquid medium viscosity,  $a$  and  $D$  are the radius and diffusion coefficient of (monosized) spherical particles at low volume fractions, and  $kT$  is the thermal energy. The quantities  $b$  and  $m$  are fitting parameters; the value  $1/b$  is the value of  $\dot{\gamma}'$  at the transition. Krieger and Dougherty (1959) and Mewis *et al.* (1989) indicated a modification in which  $\dot{\gamma}'$  is replaced by a dimensionless shear stress  $\tau' = \eta \dot{\gamma}_m a^3 / kT$ . Only at high volume fractions  $\Phi (> 0.5-0.6)$  must a value of  $m$  differing from unity be taken (Mewis *et al.*, 1989) in order to agree reasonably with experimental results.

Krieger (1972) and Choi and Krieger (1986) claimed that in the range  $0.3 < \Phi < 0.5$   $b$  can be taken constant. Note however that their

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tests, plots of  $\eta$  vs  $\log(\tau')$ , are rather insensitive to changes in  $b$ . Several experimental studies (Maron *et al.*, 1955a, 1955b; Mewis *et al.*, 1989; de Kruif *et al.*, 1985; van der Werff, 1989a) as well as theoretical ones (Russel and Gast, 1986) indicate that this, generally speaking, is not valid. Van der Werff *et al.* (1989b) argue that due to the diffusion relaxation process involved one should, in the definition of  $\tau'$ , use a diffusion coefficient corresponding with time scales between those of the short and the long range self-diffusion coefficient at that specific volume fraction. Because a series of relaxation times is involved the choice of the proper diffusion coefficient is unclear.

At low volume fraction the transition from Brownian to hydrodynamic dominance usually is described by the Péclet number, either based on shear rates ( $Pe_r = 6\pi\eta_0 a^3 \dot{\gamma}_{m,t}/kT$ ) or on shear stresses ( $Pe_r = 6\pi a^3 \tau_t/kT = 6\pi\tau'$ ); the index  $t$  refers to the transition. Application of these definitions to higher volume fractions makes the Péclet numbers at that transition to diverge from a value of the order unity:  $Pe_r$  decreases while  $Pe_r$  increases. Our aim is to find a Pe number which is insensitive to  $\Phi$ .

The Péclet number basically balances the viscous and Brownian contributions in the nondimensionalized momentum balance. A problem is that in a dispersion, at a given macroscopic simple shear rate  $\dot{\gamma}_m$  (with rate of strain components  $\dot{\gamma}_{12} = \dot{\gamma}_{21} = \dot{\gamma}_m$ ; all other  $\dot{\gamma}_{ij} = 0$ ), a large variety in local deformation rates and their corresponding viscous stresses occur. Taking the linear average of the rate of deformation in the liquid phase  $L$  ( $\overline{\dot{\gamma}_{L,12}} = \dot{\gamma}_m/(1 - \Phi)$ , all other  $\overline{\dot{\gamma}_{L,ij}} = 0$ ) does not reflect the variations in  $\dot{\gamma}$ ; positive and negative values of the (1,2) component compensate each other to a large extent and for the other components they compensate exactly.

A squared summation of local deformation rates via the use of the second invariant of the rate of strain tensor  $\dot{\gamma}^2 = (\dot{\gamma}:\dot{\gamma})$  is a more proper method in order to account for these variations. An additional advantage of this squared measure of the strain rates is that it can easily be related to experimental data, by calculating the viscous dissipation in a dispersion in two alternative ways (Laven *et al.*, 1991). This results in

$$(1 - \Phi)\eta_0\overline{\dot{\gamma}_L^2} = \eta\dot{\gamma}_m^2,$$

where the last factor on the left side stands for the second invariant of the rate of strain tensor as averaged over the liquid phase.

Thus we define the Péclet number based on the shear stresses and shear rates in the liquid ("L") phase:

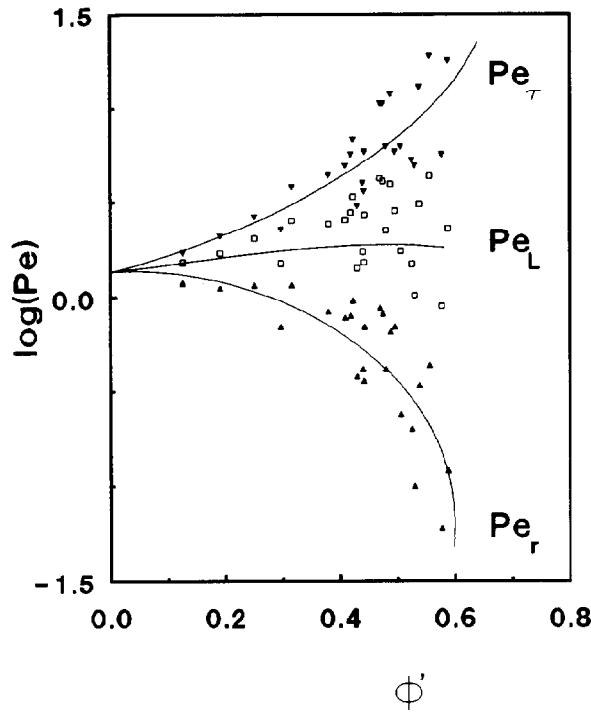


FIG. 1. Values of the three Péclet numbers discussed in the text for the transition from the Brownian to the hydrodynamic regime in hard-spheres dispersions (particle diameters 48, 77, and 115–130 nm), as calculated and taken from van der Werff (1989a).

$$Pe_L = 6\pi\eta_0 a^3 (\dot{\gamma}_L^2)^{1/2} / kT.$$

In the literature only  $Pe_r$  and/or  $Pe_\tau$  are given.  $Pe_L$  can be derived from these quantities in the following way:

$$(Pe_L)^2 = \left(\frac{6\pi a^3}{kT}\right)^2 \eta_0^2 \dot{\gamma}_L^2 = \left(\frac{6\pi a^3}{kT}\right)^2 \eta_0 \frac{\eta \dot{\gamma}_m^2}{1-\Phi} = \frac{Pe_r Pe_\tau}{1-\Phi}.$$

Finally we apply the newly-defined Péclet number in the interpretation of two sets of data on the Brownian-hydrodynamic transition, as given by Mewis *et al.* (1989) and van der Werff *et al.* (1989a). From their data we calculated or obtained values for the three Péclet numbers discussed. The results, on logarithmic coordinates, are plotted in Figs. 1

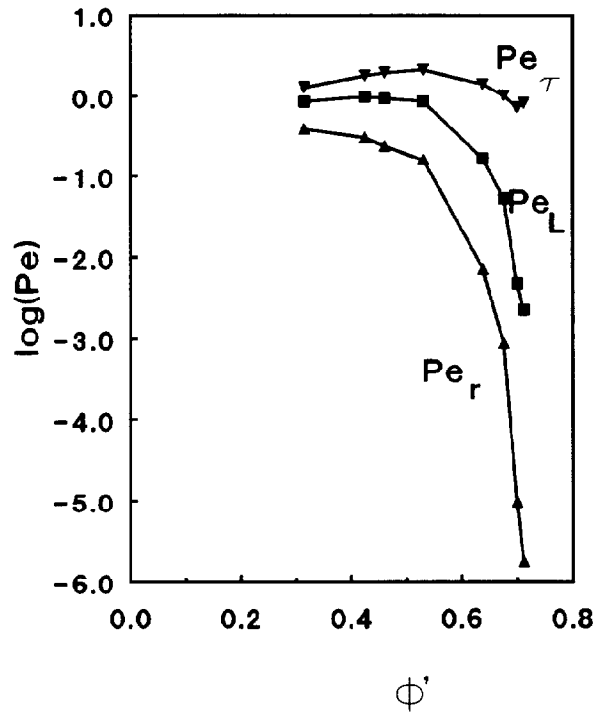


FIG. 2. Values of the three Péclet numbers discussed in the text for the transition from the Brownian to the hydrodynamic regime in hard-spheres dispersions (particle diameter 84 nm), as calculated and taken from Mewis *et al.* (1989).

and 2. The  $Pe$  values in Figs. 1 and 2 show similar magnitudes and dependences on the effective volume fraction  $\Phi'$  ( $\Phi'$  is the sum of the volume fractions of the cores and the hairy layers). It is evident that, in Fig. 1,  $Pe_L$  is by far the most constant of the three Péclet numbers.

However, at the highest volume fractions, at concentrations at which the hairy layers of the sterically stabilized particles have much interaction, also  $Pe_L$  diverges from  $O(1)$ . These high effective volume fractions ( $\geq 0.6$ ) were only accessible (i.e., they have finite viscosities) with the smaller particles [with diameters  $< 130$  nm; not with diameters  $\geq 475$  nm (Mewis, 1989)] in which case a considerable part of the effective volume fraction of the particles is due to the hairy layers. Sharp deviations of  $Pe_L$  at high  $\Phi'$  might be due to overlap or compression of hairy layers

of neighboring particles at these very high volume fractions. This seems to be reflected also in the exceptionally high values of the extrapolated maximum effective volume fractions (Mewis *et al.*, 1989; van der Werff and de Kruif, 1989a).

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