Problem 1B.3

Viscosity of suspensions. Data of Vand[3] for suspensions of small glass spheres in aqueous glycerol solutions of ZnI_2 can be represented up to about $\phi = 0.5$ by the semiempirical expression

$$\frac{\mu_{\text{eff}}}{\mu_0} = 1 + 2.5\phi + 7.17\phi^2 + 16.2\phi^3 + \cdots \tag{1B.3-1}$$

Compare this result with Eq. 1.6-2.

Answer: The Mooney equation gives a good fit of Vand's data if ϕ_0 is assigned the very reasonable value of 0.70.

Solution

Eq. 1.6-2 is the Mooney equation,

$$\frac{\mu_{\text{eff}}}{\mu_0} = \exp\left(\frac{\frac{5}{2}\phi}{1 - (\phi/\phi_0)}\right).$$

Expand the exponential function in a Taylor series centered at $\phi = 0$.

$$\exp x = 1 + x + \frac{1}{2!}x^2 + \frac{1}{3!}x^3 + \cdots ,$$

Substitute the argument of the exponential for x, so we have

$$\begin{aligned}\frac{\mu_{\text{eff}}}{\mu_0} &= 1 + \frac{\frac{5}{2}\phi}{1 - (\phi/\phi_0)} + \frac{1}{2}\left[\frac{\frac{5}{2}\phi}{1 - (\phi/\phi_0)}\right]^2 + \frac{1}{6}\left[\frac{\frac{5}{2}\phi}{1 - (\phi/\phi_0)}\right]^3 + \cdots \\ &= 1 + \frac{5}{2}\phi[1 - (\phi/\phi_0)]^{-1} + \frac{1}{2}\cdot\frac{25}{4}\phi^2[1 - (\phi/\phi_0)]^{-2} + \frac{1}{6}\cdot\frac{125}{8}\phi^3[1 - (\phi/\phi_0)]^{-3} + \cdots\end{aligned}$$

Use the binomial theorem.

$$= 1 + \frac{5}{2}\phi[1 + (\phi/\phi_0) + (\phi/\phi_0)^2 + \cdots] + \frac{1}{2}\cdot\frac{25}{4}\phi^2[1 + 2(\phi/\phi_0) + \cdots] + \frac{1}{6}\cdot\frac{125}{8}\phi^3(1 + \cdots) + \cdots$$

Expand all the terms.

$$= 1 + \frac{5}{2}\phi + \frac{5}{2\phi_0^2}\phi^3 + \frac{25}{8}\phi^2 + \frac{25}{4\phi_0}\phi^3 + \frac{125}{48}\phi^3 + \cdots$$

Factor the expression in powers of ϕ.

$$= 1 + \frac{5}{2}\phi + \left(\frac{25}{8} + \frac{5}{2\phi_0}\right)\phi^2 + \left(\frac{125}{48} + \frac{25}{4\phi_0} + \frac{5}{2\phi_0^2}\right)\phi^3 + \cdots$$

Set

$$\frac{25}{8} + \frac{5}{2\phi_0} = 7.17 \quad \text{and} \quad \frac{125}{48} + \frac{25}{4\phi_0} + \frac{5}{2\phi_0^2} = 16.2.$$

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[3] V. Vand, *J. Phys. Colloid Chem.,* **52**, 277–299, 300–314, 314–321 (1948).

There's only one unknown but two equations, so we resort to the method of least squares. We want to choose the value of ϕ_0 that minimizes the sum of the squares of the differences.

$$\left[7.17 - \left(\frac{25}{8} + \frac{5}{2\phi_0}\right)\right]^2 + \left[16.2 - \left(\frac{125}{48} + \frac{25}{4\phi_0} + \frac{5}{2\phi_0^2}\right)\right]^2$$

In order to do so, take the derivative with respect to ϕ_0 and set it equal to zero.

$$2\left[7.17 - \left(\frac{25}{8} + \frac{5}{2\phi_0}\right)\right]\left(\frac{5}{2\phi_0^2}\right) + 2\left[16.2 - \left(\frac{125}{48} + \frac{25}{4\phi_0} + \frac{5}{2\phi_0^2}\right)\right]\left(\frac{25}{4\phi_0^2} + \frac{5}{\phi_0^3}\right) = 0$$

Expand all the terms.

$$\frac{190.73}{\phi_0^2} + \frac{45.3333}{\phi_0^3} - \frac{375}{4\phi_0^4} - \frac{25}{\phi_0^5} = 0$$

Multiply both sides by ϕ_0^5.

$$190.73\phi_0^3 + 45.3333\phi_0^2 - \frac{375}{4}\phi_0 - 25 = 0$$

The solution to this cubic equation is $\phi_0 \approx \{-0.67922, -0.271646, 0.712487\}$. We choose ϕ_0 to be the positive value.

$$\boxed{\phi_0 \approx 0.7125}$$

When ϕ_0 takes this value, the Mooney equation therefore becomes

$$\frac{\mu_{\text{eff}}}{\mu_0} = 1 + 2.5\phi + 6.63\phi^2 + 16.3\phi^3 + \cdots.$$

The first two terms are the same as the Vand equation. The other two have the following percent differences.

$$\phi^2 \text{ Coefficient Percent Difference}: \quad \frac{6.63 - 7.17}{7.17} \times 100\% \approx -7.48\%$$
$$\phi^3 \text{ Coefficient Percent Difference}: \quad \frac{16.3 - 16.2}{16.2} \times 100\% \approx 0.617\%$$

The coefficient of ϕ^2 in the Mooney equation is below that in the Vand equation by 7.48%, and the coefficient of ϕ^3 is above that in the Vand equation by 0.617%.