Suspensions and polymer solutions

Solution of Exercise 4

1. We begin by inverting the first term in $\tilde{G}_{ij}$, which is proportional to $1/q^2$.

$$\mathcal{F}^{-1}\left[\frac{1}{q^2}\right] = \frac{1}{(2\pi)^3}\int d^3q e^{i\vec{q}\cdot\vec{r}}\frac{1}{q^2} = \frac{1}{(2\pi)^3}\int_0^\infty dq \int_{-1}^{1} d(\cos\theta)\int_0^{2\pi} d\varphi e^{iqr\cos\theta}$$
$$= \frac{1}{2\pi^2}\int_0^\infty dq\frac{\sin(qr)}{qr} = \frac{1}{2\pi^2 r}\int_0^\infty du\frac{\sin u}{u} = \frac{1}{4\pi r}. \quad (1)$$

Similarly, if we invert $1/q^4$ we will get $(2\pi^2)^{-1}\int_0^\infty dq\sin(qr)/(q^3r)$. This integral diverges at $q\to 0$, but we note that for the second term in $\tilde{G}_{ij}$ we actually need to invert q_iq_j/q^4, which removes this divergence.

$$\mathcal{F}^{-1}\left[\frac{-q_iq_j}{q^4}\right] = \partial_i\partial_j\mathcal{F}^{-1}\left[\frac{1}{q^4}\right] = \frac{1}{2\pi^2}\partial_i\partial_j\int_0^\infty dq\frac{\sin(qr)}{q^3r} = \dots$$
$$= \frac{1}{2\pi^2}\int_0^\infty dq\left\{\left[\frac{\cos(qr)}{(qr)^2}-\frac{\sin(qr)}{(qr)^3}\right]\delta_{ij} - \left[\frac{\sin(qr)}{qr}+3\left(\frac{\cos(qr)}{(qr)^2}-\frac{\sin(qr)}{(qr)^3}\right)\right]\frac{r_ir_j}{r^2}\right\}. \quad (2)$$

The integral $\int_0^\infty dq\sin(qr)/(qr) = \pi/(2r)$ has already been calculated in Eq. (1). The other one needed is

$$\int_0^\infty dq\left[\frac{\cos(qr)}{(qr)^2}-\frac{\sin(qr)}{(qr)^3}\right] = \frac{1}{r}\int_0^\infty du\left(\frac{\cos u}{u^2}-\frac{\sin u}{u^3}\right) = -\frac{\pi}{4r}.$$

Substituting these two results in Eq. (2) gives

$$\mathcal{F}^{-1}\left[\frac{-q_iq_j}{q^4}\right] = \frac{1}{8\pi r}\left(-\delta_{ij}+\frac{r_ir_j}{r^2}\right). \quad (3)$$

Finally, using Eqs. (1) and (3) in the expression for $\tilde{G}_{ij}$, we find,

$$G_{ij}(\vec{r}) = \mathcal{F}^{-1}\left[\tilde{G}_{ij}(\vec{q})\right] = \frac{1}{8\pi\eta r}\left(\delta_{ij}+\frac{r_ir_j}{r^2}\right). \quad (4)$$

2. From the definition of $\mathbf{r}_{\rm CM}$ we have

$$\langle r_{\rm CM}^2\rangle = \frac{1}{4}\langle(r^{(1)})^2\rangle + \frac{1}{4}\langle(r^{(2)})^2\rangle + \frac{1}{2}\langle\mathbf{r}^{(1)}\cdot\mathbf{r}^{(2)}\rangle. \quad (5)$$

   (a) In the absence of hydrodynamic interactions the motions of the two particles are independent, i.e., $\langle\mathbf{r}^{(1)}\cdot\mathbf{r}^{(2)}\rangle = 0$. We then find from Eq. (5) $6D_{\rm CM} = (2/4)6D_{\rm s}$, i.e.,

$$D_{\rm CM} = \frac{1}{2}D_{\rm s} = \frac{k_{\rm B}T}{12\pi\eta a}. \quad (6)$$

   We see that the diffusivity of the center of mass is smaller (by a factor of 1/2) than that of the single particles. This makes sense, because $D_{\rm CM}$ characterizes the diffusion of a larger, less mobile object — a particle pair. You can easily verify that the same calculation for N uncorrelated particles will yield $D_{\rm CM} = D_{\rm s}/N$.

(b) In the limit $r \gg a$ we may assume (i) that the self-diffusion of a single particle is unaffected by the presence of the other; and (ii) that the coupling diffusion coefficients, as we showed in class, are given by $k_{\rm B}T$ times the appropriate components of the Oseen tensor. Assumption (i) leads to

$$\langle (r^{(1)})^2 \rangle = \langle (r^{(2)})^2 \rangle = 6D_{\rm s}t = \frac{k_{\rm B}T}{\pi\eta a},$$

and assumption (ii) to

$$\begin{aligned}\langle \mathbf{r}^{(1)} \cdot \mathbf{r}^{(2)} \rangle &= \langle x^{(1)}x^{(2)} \rangle + \langle y^{(1)}y^{(2)} \rangle + \langle z^{(1)}z^{(2)} \rangle = 2D^{12}_{xx}t + 2D^{12}_{yy}t + 2D^{12}_{zz}t \\ &= 2k_{\rm B}T[G_{xx}(r\hat{\mathbf{x}}) + G_{yy}(r\hat{\mathbf{x}}) + G_{zz}(r\hat{\mathbf{x}})]t = 2k_{\rm B}T\left(\frac{1}{4\pi\eta r} + \frac{1}{8\pi\eta r} + \frac{1}{8\pi\eta r}\right)t \\ &= \frac{k_{\rm B}T}{\pi\eta r}t.\end{aligned}$$

Substituting these two results in Eq. (5), we find

$$\langle r^2_{\rm CM} \rangle = \left(\frac{k_{\rm B}T}{4\pi\eta a} + \frac{k_{\rm B}T}{4\pi\eta a} + \frac{k_{\rm B}T}{2\pi\eta r}\right)t = \frac{k_{\rm B}T}{2\pi\eta a}\left(1 + \frac{a}{r}\right)t,$$

namely,

$$D_{\rm CM} = \frac{k_{\rm B}T}{12\pi\eta a}\left(1 + \frac{a}{r}\right). \tag{7}$$

For $r \to \infty$ the hydrodynamic interaction vanishes, the particles become uncorrelated, and Eq. (7) coincides with Eq. (6) of item (a), as expected. At finite r, however, the hydrodynamic interaction leads to a correction of order a/r, which *enhances* the diffusion of the center of mass. This is because the hydrodynamic interaction makes particles drag one another in the same direction, making the pair move more as a coherent body.

(c) The correction in Eq. (7) is larger than 10% when $a/r > 0.1$, i.e., for $r < 10a$. At particle concentration c the mean inter-particle distance is $c^{-1/3}$. We therefore expect deviations of order 10% when $c > 1/(10a)^3 = 10^{-3}\ a^{-3}$. The volume fraction is related to concentration as $\phi = c(4\pi a^3/3)$. So deviations of order 10% are expected for $\phi > 4\pi/(3{\cdot}10^3) \simeq 4.2\times 10^{-3}$. We see that hydrodynamic interactions become important for the dynamics of suspensions already at very low volume fraction! This is a consequence of the long range of the interaction. Note another interesting consequence of the long-range (scale-free) nature of the Oseen tensor: these qualitative conclusions are parameter-free — they do not depend on η or a.