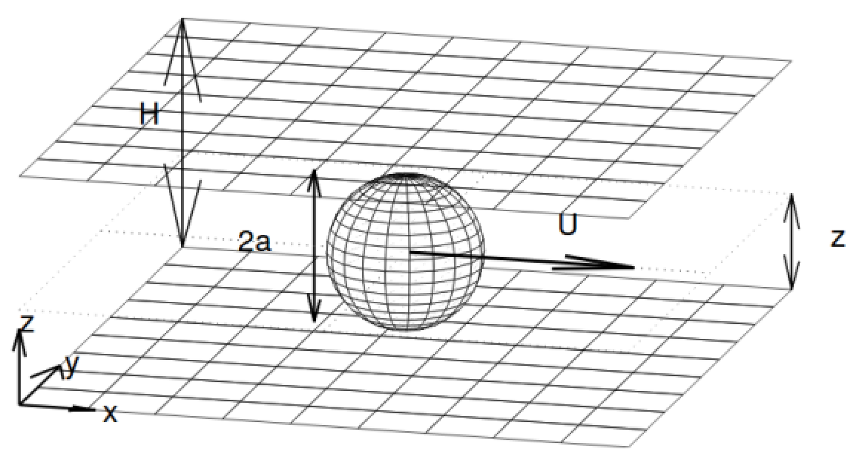
DIFFUSION COEFFICIENT IN CONFINED ENVIRONMENT WITH PBC CONDITIONS

Anne-Francoise de Guerny(LJLL), Jean-Francois Dufreche(ICSM),
Yvon Maday(LJLL), Jean-Philip Piquemal(LCT)

Abstract

We study the system-size dependence and the influence of the boundary conditions for diffusion coefficient D of a particule moving in a confined fluid between two planes quite far away. That work is motivated by the study of molecular dynamics simulations which often use periodic boundary conditions in order to simulate a system with a physical meaning.



Model Formulation

$$\begin{cases} \eta\Delta\mathbf{u}(x,y,z) = \triangledown p(x,y,z) - \delta(x,y,z)\mathbf{F} \\ \triangledown.\mathbf{u}(x,y,z) = 0 \end{cases} \tag{1}$$

where $(x,y,z) \in \mathbb{R}^2 \times \left[-\frac{H}{2}, \frac{H}{2}\right]$, δ is the dirac distribution centered in zero

On both walls and for $(x,y) \in \mathbb{R}^2$

$$\mathbf{u}\left(x, y, \pm\frac{H}{2}\right) = (0,0,0) \tag{2}$$

Conclusion

We first derive a simple analytic-correction for the diffusion coefficient of a system composed by a particule moving in a fluid with slab geometry. We then see the major influence of the periodic boundary conditions and then the correction to be made in this requirement. In both cases, we note that the diffusion coefficient that we obtain converge to the one's in the Stoke's Problem solved in $\mathbb{R}^3 \setminus B(0,a)$ with non-periodical conditions (i.e. when $H \to \infty$ in the first case, and when also $L \to \infty$ in the second one, we get $D \to D_0$).

References

[1] A.Saugey, L.Joly, C.Ybert, J-L.Barrat, L.Bocquet, Diffusion in pores and its dependence on boundary conditions, Journal Of Physics-Condensed Matter, 2005

[2] I-C.Yeh, G.Hummer, System-Size Dependence of Diffusion Coefficients and Viscosities from Molecular Dynamics Simulations with Periodic Boundary Conditions, J. Phys. Chem., 2004

[3] M.Lisicki, Four approaches to hydrodynamic Green's functions - the Oseen tensors

[4] J.G.Kirwood, J.Riseman, The Intrinsic Viscosities and Diffusion Constants of Flexible Macromolecules in Solution, J. Chem. Phys., 1948

Non periodical case

Theorem 1. *$\boldsymbol{u}$ is of the form*

$$\begin{aligned} \boldsymbol{u}(x,y,z) &= \boldsymbol{T}_1(x,y,z).\boldsymbol{F} \\ &= \int d\boldsymbol{k}\Bigg(\Bigg(A_1(\boldsymbol{k})(z)\begin{pmatrix}1&0&0\\0&1&0\\0&0&0\end{pmatrix} + A_2(\boldsymbol{k})(z)\begin{pmatrix}0&0&0\\0&0&0\\0&0&1\end{pmatrix} + A_3(\boldsymbol{k})(z)\boldsymbol{k}'\otimes\boldsymbol{k}'\Bigg) \\ &+ i\Bigg(A_4(\boldsymbol{k})(z)\begin{pmatrix}0&0&0\\0&0&0\\0&0&1\end{pmatrix} + A_5(\boldsymbol{k})(z)\begin{pmatrix}0&0&k_1\\0&0&k_2\\0&0&0\end{pmatrix} + A_6(\boldsymbol{k})(z)\begin{pmatrix}0&0&0\\0&0&0\\k_1&k_2&0\end{pmatrix}\Bigg)\Bigg)e^{i\boldsymbol{k}.(x,y)}.\boldsymbol{F} \end{aligned} \tag{3}$$

with $A_i(\boldsymbol{k}) = f_i(H, \cosh(\|\boldsymbol{k}\|\frac{H}{2}), \sinh(\|\boldsymbol{k}\|\frac{H}{2}))$ $(i = 1, ..., 6)$

Proof. (key elements) We use the Fourier Transform in two dimension so that we get

$$\begin{cases} \eta\left(\widehat{u_1}(\mathbf{k})''(z) - \|\mathbf{k}\|^2\widehat{u_1}(\mathbf{k})(z)\right) = ik_1\widehat{p}(\mathbf{k})(z) - \widehat{\delta}(\mathbf{k})(z)F_1 \\ \eta\left(\widehat{u_2}(\mathbf{k})''(z) - \|\mathbf{k}\|^2\widehat{u_2}(\mathbf{k})(z)\right) = ik_2\widehat{p}(\mathbf{k})(z) - \widehat{\delta}(\mathbf{k})(z)F_2 \\ \eta\left(\widehat{u_3}(\mathbf{k})''(z) - \|\mathbf{k}\|^2\widehat{u_3}(\mathbf{k})(z)\right) = \widehat{p}(\mathbf{k})'(z) - \widehat{\delta}(\mathbf{k})(z)F_3 \\ ik_1\widehat{u_1}(\mathbf{k})(z) + ik_2\widehat{u_2}(\mathbf{k})(z) + \widehat{u_3}(\mathbf{k})'(z) = 0 \end{cases} \tag{4}$$

We make the same by taking the divergenge of the first equation so that we obtain

$$\widehat{p}(\mathbf{k})''(z) - \|\mathbf{k}\|^2\widehat{p}(\mathbf{k})(z) = i\left(k_1F_1 + k_2F_2\right)\widehat{\delta}(\mathbf{k})(z) + F_3\widehat{\delta}(\mathbf{k})'(z) \tag{5}$$

That is, for (3) and (4), ODE in z with distribution. □

Theorem 2. *When H is large enough we have*

$$\begin{aligned} D &= D_0 + \frac{kT}{3}\lim_{\|(x,y,z)\|\to 0} Tr(\boldsymbol{T}_1(x,y,z) - \boldsymbol{T}_{Oseen}(x,y,z)) \\ &= D_0 - \frac{CkT}{8\pi H\eta} + o\left(\frac{1}{H}\right) \end{aligned} \tag{6}$$

$$\left(D_0 = \frac{kT}{6\pi\eta a},\ \text{and}\ \boldsymbol{T}_{Oseen}(x,y,z) = \frac{1}{8\pi\eta\|(x,y,z)\|}\left(\boldsymbol{I}_3 + \frac{(x,y,z)\otimes(x,y,z)}{\|(x,y,z)\|^2}\right)\right)$$

This result is in good agreement with the development that we can obtain with the one's from Saugey and al., when we take H large enought.

Calculus in the PBC case

Theorem 3. *$\boldsymbol{u}$ is of the form*

$$\begin{aligned} \boldsymbol{u}(x,y,z) &= \boldsymbol{T}_2(x,y,z).\boldsymbol{F} \\ &= \frac{1}{L^2}A_0(0,0)(z)\begin{pmatrix}1&0&0\\0&1&0\\0&0&0\end{pmatrix}.\boldsymbol{F} + \frac{1}{L^2}\sum_{\boldsymbol{k}\neq 0}\Bigg(\Bigg(A_1(\boldsymbol{k})(z)\begin{pmatrix}1&0&0\\0&1&0\\0&0&0\end{pmatrix} + A_2(\boldsymbol{k})(z)\begin{pmatrix}0&0&0\\0&0&0\\0&0&1\end{pmatrix} \\ &+ A_3(\boldsymbol{k})(z)\boldsymbol{k}'\otimes\boldsymbol{k}'\Bigg) + i\Bigg(A_4(\boldsymbol{k})(z)\begin{pmatrix}0&0&k_1\\0&0&k_2\\0&0&0\end{pmatrix} + A_5(\boldsymbol{k})(z)\begin{pmatrix}0&0&0\\0&0&0\\k_1&k_2&0\end{pmatrix}\Bigg)\Bigg)e^{i\boldsymbol{k}.(x,y)}.\boldsymbol{F} \end{aligned} \tag{7}$$

where $\boldsymbol{k} = 2\pi(\frac{m_1}{L}, \frac{m_2}{L})$ with $(m_1, m_2) \in \mathbb{Z}^2$, and where A_i $(i = 1, ..., 6)$ are given in theorem 1 and $A_0(0,0)(z) = \left(\frac{1}{2\eta}z - \frac{z}{\eta}\mathbf{1}_{z\geq 0} + \frac{H}{4\eta}\right)$

Theorem 4. *When H is large enough we have*

$$\begin{aligned} D &= D_0 + \frac{kT}{3}\lim_{\|(x,y,z)\|\to 0} Tr(\boldsymbol{T}_2(x,y,z) - \boldsymbol{T}_{Oseen}(x,y,z)) \\ &= D_0 + \frac{kT}{3}\Bigg(\frac{H}{8L^2\eta} + \frac{1}{\eta L}\sum_{\boldsymbol{n}\neq(0,0)}\left(\frac{1}{2\pi\|\boldsymbol{n}\|} - \frac{1}{2\pi\|\boldsymbol{n}\|} * \frac{\alpha^2}{\pi}e^{-\alpha^2\|\boldsymbol{n}L\|^2}\right) + \frac{1}{\eta L^2}\sum_{\boldsymbol{k}\neq 0}\frac{1}{\|\boldsymbol{k}\|}e^{-\frac{\boldsymbol{k}^2}{4\alpha^2}} \\ &- \frac{\alpha}{2\pi^{1/2}} + \frac{1}{L^2}\sum_{\boldsymbol{k}\neq 0}\left(\frac{-2}{e^{\|\boldsymbol{k}\|\frac{H}{2}}\|\boldsymbol{k}\|\eta} - \frac{\|\boldsymbol{k}\|H^2}{4e^{\|\boldsymbol{k}\|H}\eta} - \frac{\|\boldsymbol{k}\|^2H^3}{2e^{2\|\boldsymbol{k}\|H}\eta}\right) + o\left(\frac{1}{L^2}\sum_{\boldsymbol{k}\neq 0}e^{-2\|\boldsymbol{k}\|H}\right) \end{aligned} \tag{8}$$

α beging an arbitrary convergence factor ($\alpha > 0$).

Proof. (key elements) The main difficulty is to treat the term $\frac{1}{\eta L^2}\sum_{\mathbf{k}\neq(0,0)}\frac{1}{\|\mathbf{k}\|}e^{i\mathbf{k}.(x,y)}$. We adapt, for that, an Ewald type method for a double (and not triple) sum. □