Aerosol Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/uast20

Rotational Diffusion Coefficient (or Rotational Mobility) of a Nanorod in the Free-Molecular Regime

Mingdong Li [a b c], George W. Mulholland [a b c] & Michael R. Zachariah [a b c]

[a] Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, Maryland, USA

[b] Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland, USA

[c] Chemical Sciences Division, National Institute of Standards and Technology, Gaithersburg, Maryland, USA

Accepted author version posted online: 14 Nov 2013.Published online: 14 Nov 2013.

To cite this article: Mingdong Li, George W. Mulholland & Michael R. Zachariah (2014) Rotational Diffusion Coefficient (or Rotational Mobility) of a Nanorod in the Free-Molecular Regime, Aerosol Science and Technology, 48:2, 139-141, DOI: 10.1080/02786826.2013.864752

To link to this article: http://dx.doi.org/10.1080/02786826.2013.864752

Aerosol Science and Technology, 48:139–141, 2014

ISSN: 0278-6826 print / 1521-7388 online
DOI: 10.1080/02786826.2013.864752

Rotational Diffusion Coefficient (or Rotational Mobility) of a Nanorod in the Free-Molecular Regime

Mingdong Li,[1,2,3] George W. Mulholland,[1,2,3] and Michael R. Zachariah[1,2,3]
[1]*Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, Maryland, USA*
[2]*Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland, USA*
[3]*Chemical Sciences Division, National Institute of Standards and Technology, Gaithersburg, Maryland, USA*

The corrected rotational diffusion coefficient for a rod in the free molecular regime is given in this work and a simplified derivation using the differential drag forces for a rotating rod in the free molecular regime is presented to explain the difference between our result and the one from Kim's approach. Finally, we compare the rotational diffusion coefficient between a rod and an ellipsoid with the same aspect ratio and the same volume.

1. INTRODUCTION

Rotational diffusion coefficient, which is related to rotational mobility, is the characteristic value of the Brownian rotation of a particle. This quantity is important in studies of the alignment of nonspherical particles in an electric field (Li 2012; Li et al. 2012, 2013a,b). The theory for rotational Brownian diffusion coefficient of dilute suspensions of axially symmetric particles in the continuum regime has been studied by a number of researchers (Brenner 1974; Brenner and Condiff 1974; Ortega and de la Torre 2003). In the free molecular regime, Halbritter (1974) calculated the rotational torque for a general convex-shaped particle and obtained an explicit torque expression for an ellipsoid (Halbritter 1974; Williams and Loyalka 1991). Eisner and Gallily (1981) calculated the rotational diffusion coefficient of nonspherical aerosol particles and obtained an explicit rotational diffusion coefficient expression for a rod. However, Eisner and Gallily (1981) did not express the moment of specular reflection correctly. In Equation (3.6) of Eisner and Gallily (1981), the velocities should be relative to the particle surface, i.e., (v_1, v_1'), instead of to the observer, (v_2, v_2')). The corrected rotational diffusion coefficient for a rod in the free molecular regime, using a common definition of rod aspect ratio $\beta = L_r/d_r$, is

$$D_{\mathrm{r,f}} = \frac{k_{\mathrm{B}} T K_n}{\pi \mu L_r^3 \left[\left(\frac{1}{6} + \frac{1}{8\beta^3} \right) + f \left(\frac{\pi-2}{48} + \frac{1}{8\beta} + \frac{1}{8\beta^2} + \frac{\pi-4}{8} \frac{1}{8\beta^3} \right) \right]}, \quad [1]$$

where k_B is the Boltzmann constant, T is the absolute temperature, the Knudsen number $K_n = 2\lambda/d_r$, λ is the mean free path of gas, d_r is the rod diameter, L_r is the rod length, μ is the gas viscosity, and f is the momentum accommodation. To compare with our result, we give Eisner and Gallily's uncorrected equation (Eisner and Gallily 1981):

$$D_{\mathrm{r,f}} = \frac{k_{\mathrm{B}} T K_{\mathrm{n}}}{\pi \mu L_r^3 \left[\left(\frac{1}{4} + \frac{1}{4\beta} + \frac{1}{4\beta^2} + \frac{1}{8\beta^3} \right) + f \left(\frac{\pi-6}{48} - \frac{1}{8\beta} - \frac{1}{8\beta^2} + \frac{\pi-4}{8} \frac{1}{8\beta^3} \right) \right]}. \quad [2]$$

The difference between the two expressions is 5–10% for a momentum accommodation, f, of 0.9 and rod aspect ratio β greater than 2.

2. DERIVATIONS AND DISCUSSIONS

The corrected rotational diffusion coefficient for a rod in the free molecular regime, i.e., Equation (1), can be obtained by repeating the derivation procedures in Eisner and Gallily (1981) but using the correct velocity relationship for specular reflection as mentioned earlier. In this work, we show another derivation for Equation (1) using the differential drag forces for a rotating rod in the free molecular regime and explain the difference

Received 26 July 2013; accepted 5 November 2013.
Address correspondence to George W. Mulholland, Mechanical Engineering, University of Maryland, 2181 Glenn L. Martin Hall, College Park, MD 20742, USA. E-mail: georgewm@umd.edu; gwm@umd.edu
Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/uast.

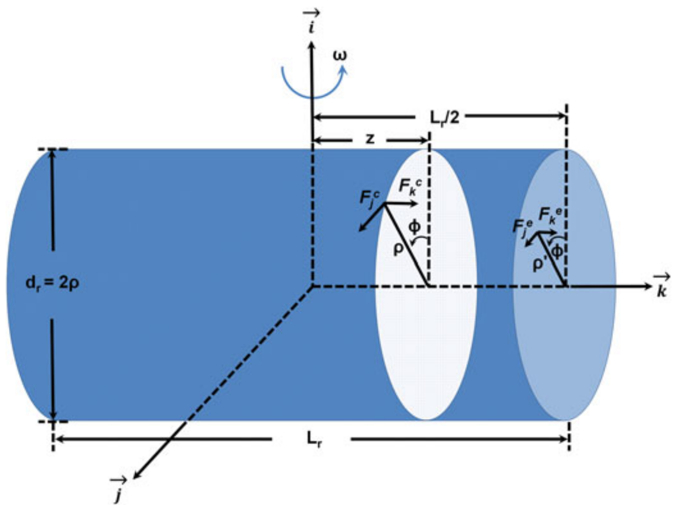

FIG. 1. A rotational rod (with angular velocity $\omega\,\vec{i}$) in a coordinate system $(\vec{i}, \vec{j}, \vec{k})$.

between our result and the one from Kim's approach (Kim et al. 2007).

Halbritter (1974) calculated the differential drag forces for a general convex particle with an angular velocity ω in the free molecular regime (Halbritter 1974, Equation 8). We apply the general equation to calculate the differential drag forces for a rotational rod with an angular velocity ω (Figure 1). Assuming that the rod (with length L_r and diameter $d_r = 2\rho$) rotates along the $\vec{i}$ axis, for a small patch on the curved portion of the cylindrical surface with coordinates ($\rho\cos\phi$, $\rho\sin\phi$, z), the differential forces along the $\vec{j}$ axis, $dF_j{}^c$, and along the $\vec{k}$ axis, $dF_k{}^c$, are

$$dF_j^c = \frac{\mu}{\lambda}\omega z\left[\left(2 - \frac{4-\pi}{4}f\right)\sin^2\phi + \frac{1}{2}f\cos^2\phi\right]dS^c, \qquad [3]$$

$$dF_k^c = -\frac{\mu}{2\lambda}f\omega\rho\sin\phi dS^c, \qquad [4]$$

where $dS^c = \rho d\phi dz$ and the integration range $-\frac{L_r}{2} \leq z \leq \frac{L_r}{2}$, $0 \leq \phi \leq 2\pi$.

For a small patch on the flat-end surface with coordinates ($\rho'\cos\phi$, $\rho'\sin\phi$, $L_r/2$), the differential forces along the $\vec{j}$ axis, $dF_j{}^e$, and along the $\vec{k}$ axis, $dF_k{}^e$, are

$$dF_j^e = \frac{\mu}{2\lambda}f\omega\frac{L_r}{2}dS^e, \qquad [5]$$

$$dF_k^e = -\left(2 - \frac{4-\pi}{4}f\right)\frac{\mu}{\lambda}\omega\rho'\sin\phi dS^e, \qquad [6]$$

where $dS^e = \rho' d\phi d\rho'$ and the integration range $0 \leq \rho' \leq \rho$, $0 \leq \phi < 2\pi$.

Then, the total torque, M, along the $\vec{i}$ axis can be obtained by considering the contribution from forces along $\vec{j}$ axis and $\vec{k}$ axis for the curved cylindrical surface (1st integral) and the two flat-end surfaces (2nd integral) as

$$\begin{aligned} M = &\int\left(-zdF_j^c + \rho\sin\phi dF_k^c\right) + 2\int\left(-\frac{L}{2}dF_j^e + \rho'\sin\phi dF_k^e\right) \\ = &\,\pi\mu L_r^3\left[\left(\frac{1}{6} + \frac{1}{8\beta^3}\right) + f\left(\frac{\pi-2}{48} + \frac{1}{8\beta} + \frac{1}{8\beta^2}\right.\right. \\ &\left.\left. + \frac{\pi-4}{8}\frac{1}{8\beta^3}\right)\right]\frac{d_r\omega}{2\lambda}. \end{aligned} \qquad [7]$$

Then, the rotational mobility is $B_\omega = \omega/M$, and the rotational diffusion coefficient is $D_{r,f} = k_B T B_\omega$, which gives Equation (1).

The differential forces parallel to the velocity direction, i.e., $dF_j{}^c$ in Equation (3) and $dF_j{}^e$ in Equation (5), are identical to the differential forces in Equation (21) of Dahneke (1973) on substituting drifting velocity $V_d = -\omega z$ and $V_d = -\omega L_r/2$, respectively. However, the differential forces perpendicular to the velocity direction for a rotational movement ($dF_k{}^c$ in Equation (4) and $dF_k{}^e$ in Equation (6), respectively) are different from the forces for a constant translational movement which are zero as given by Dahneke (1973).

2.1. Comparing our Result in Equation (1) with Kim's Approach

In the free molecular regime, Kim et al. (2007) used a much simpler but approximate method to obtain the rotational diffusion coefficient of a rod by applying the drag forces from Dahneke (1973). Since Dahneke's drag force expressions were presented for a rod with a constant translational movement as we discussed earlier, Kim's approach calculated the torque from the forces parallel to the velocity direction, but did not consider the torque from the forces perpendicular to the velocity direction. Even though the sum of the forces perpendicular to the velocity direction is zero, the sum of the torque from those forces is not zero. However, if the rod diameter is much smaller than the length, i.e., for $1/\beta$ small, the torque from the forces perpendicular to the velocity direction can be neglected, which makes Kim's approach a good approximation for a slender rod. After correcting the missing factor of "2" (Kim et al. considered the rotational resistance of only half of the rod), and considering the effect of the two ends of the rod using Kim's approach, we obtain

$$D_{\mathrm{r,f}} = \frac{k_{\mathrm{B}}TK_{\mathrm{n}}}{\pi\mu L_r^3\left[\frac{1}{6} + f\left(\frac{\pi-2}{48} + \frac{1}{8\beta}\right)\right]}. \qquad [8]$$

To order $1/\beta$, Equations (8) and (1) are identical.

2.2. Comparing the Rotational Diffusion Coefficient Between a Rod in Equation (1) and an Ellipsoid

We make use of the explicit expression for the torque of an ellipsoid (Equation 13 of Halbritter, 1974) to compute its rotational diffusion coefficient, and compare it with Equation (1). The ratio between the rotational diffusion coefficient of an

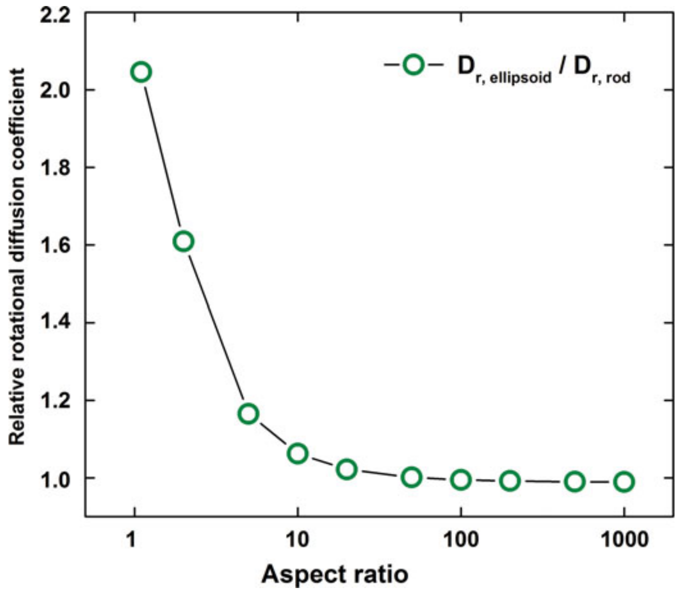

FIG. 2. Rotational diffusion coefficient ratio between an ellipsoid and a rod with the same volume and the same aspect ratio for a rod diameter $d_r = 15$ nm.

ellipsoid and a rod with the same volume and the same aspect ratio is plotted in Figure 2 assuming a rod diameter $d_r = 15$ nm and a momentum accommodation $f = 0.9$. The difference in the rotational diffusion coefficients for a rod and an ellipsoid with the same aspect ratio and same volume is less than 2.2% for aspect ratios larger than 20.

3. CONCLUSIONS

The corrected rotational diffusion coefficient for a rod in the free molecular regime is given in this work and a simplified derivation using the differential drag forces for a rotating rod in the free molecular regime is presented to explain the difference between our result and the one from Kim's approach (Kim et al. 2007). Finally, we compare the rotational diffusion coefficient between a rod and an ellipsoid with the same aspect ratio and the same volume.

REFERENCES

Brenner, H. (1974). Rheology of a Dilute Suspension of Axisymmetric Brownian Particles. *Int. J. Multiphase Flow*, 1:195–341.

Brenner, H., and Condiff, D. W. (1974). Transport Mechanics in Systems of Orientable Particles .4. Convective Transport. *J. Colloid. Interf. Sci*., 47:199–264.

Dahneke, B. E. (1973). Slip Correction Factors for Nonspherical Bodies—II Free Molecule Flow. *J. Aerosol Sci*., 4:147–161

Eisner, A. D., and Gallily, I. (1981). On the Stochastic Nature of the Motion of Nonspherical Aerosol-Particles .3. The Rotational Diffusion Diadic and Applications. *J. Colloid. Interf. Sci*., 81:214–233.

Halbritter, J. (1974), Torque on a Rotating Ellipsoid in a Rarefied-Gas. *Zeitschrift Fur Naturforschung Section a—Journal of Physical Sciences A* 29(12), 1717–1722.

Kim, S. H., Mulholland, G. W., and Zachariah, M. R. (2007). Understanding Ion-Mobility and Transport Properties of Aerosol Nanowires. *J. Aerosol Sci*., 38:823–842.

Li, M. (2012). Quantifying Particle Properties from Ion-Mobility Measurements. in *Chemical Physics Program*, Dissertation, University of Maryland, College Park. Available online at: http://hdl.handle.net/1903/13627.

Li, M., Mulholland, G. W., and Zachariah, M. R. (2012). The Effect of Orientation on the Mobility and Dynamic Shape Factor of Charged Axially Symmetric Particles in an Electric Field. *Aerosol Sci. Technol*., 46:1035–1044.

Li, M., You, R., Mulholland, G. W., and Zachariah, M. R. (2013a). Evaluating the Mobility of Nanorods in Electric Fields. *Aerosol Sci. Technol*., 47:1101–1107..

Li, M., You, R., Mulholland, G. W., and Zachariah, M. R. (2013b). Development of a Pulsed-Field Differential Mobility Analyzer: A Method for Measuring Shape Parameters for Non-Spherical Particles. *Aerosol Sci. Technol*., 48 22–30.

Ortega, A., and de la Torre, J. G. (2003). Hydrodynamic Properties of Rodlike and Disklike Particles in Dilute Solution. *J. Chem. Phys*., 119:9914–9919.

Williams, M. M. R.; Loyalka, S. K. (1991) *Aerosol Science: Theory and Practice: With Special Applications to the Nuclear Industry.* 1st ed. Pergamon Press, Oxford, 446 p.