Expressions for mean squared displacement on some curved surfaces

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This document contains derivations of the MSD $\langle \delta x \rangle^2$ on some curved surfaces. These are checked against what our fix combined with LAMMPS' fix langevin produces.

1 Cylinder

On a cylinder the MSD is the combination of a regular 1D MSD along the z-axis and the 2D MSD along a circle in the other direction. The 1D regular MSD is obviously given by $\langle \delta z \rangle = 2Dt$. For the MSD-part associated with diffusion along the circle we first solve the ϕ-part of the diffusion equation in cylindrical coordinates for a density $n(\phi, t)$:

$$D\frac{1}{R^2}\frac{\partial^2 n}{\partial \phi^2} = \frac{\partial n}{\partial t}, \qquad n(\phi) = n(\phi + 2\pi)$$

This equation has a general solution

$$n(\phi, t) = \sum_{l=0}^{\infty} A_l \cos(l\phi)\, e^{-l^2 Dt/R^2}.$$

Assuming that the initial distribution of particles is δ-distributed, $n(t = 0) = n_0\delta(\phi)/R$, we can find the coefficients A_l :

$$R\int_{\phi=0}^{\phi=2\pi} n_0(\phi)\cos(l'\phi)\,d\phi = R\int_{\phi=0}^{\phi=2\pi}\sum_{l=0}^{\infty} A_l \cos(l\phi)\cos(l'\phi)\,d\phi.$$

The left term is easily integrated using the δ-property:

$$R\int_{\phi=0}^{\phi=2\pi} n_0(\phi)\cos(l'\phi)\,d\phi = R\int_{\phi=0}^{\phi=2\pi}\frac{n_0}{R}\delta(\phi)\cos(l'\phi) = n_0$$

The second term of the integral can be rewritten as

$$R\sum_{l=0}^{\infty} A_l \int_{\phi=0}^{\phi=2\pi}\cos(l\phi)\cos(l'\phi)\,d\phi =$$
$$R\sum_{l=0}^{\infty} A_l \int_{\phi=0}^{\phi=2\pi}\delta_{ll'}\cos^2(l'\phi)\,d\phi = \begin{cases} R\pi A_l, & \text{if } l > 0 \\ 2R\pi A_0, & \text{if } l = 0 \end{cases}$$

Thus we find for $n(\phi, t)$ that

$$\begin{aligned} n(\phi, t) =& \frac{n_0}{\pi R} \sum_{l=0}^{\infty} \frac{1}{1+\delta_{l0}} \cos(l\phi) \exp\left[-l^2 \frac{Dt}{R^2}\right] \\ =& \frac{n_0}{\pi R} \left\{ \frac{1}{2} + \sum_{l=1}^{\infty} \cos(l\phi) \exp\left[-l^2 \frac{Dt}{R^2}\right] \right\} \end{aligned}$$

In figure **??** we plot this density for a few times. Since the density evolution is given by $n(\phi, t)$, the probability density function for the position of a particle is given by $p(\phi, t) = n(\phi, t)/n_0$:

$$p(\phi, t) = \frac{1}{\pi R} \left\{ \frac{1}{2} + \sum_{l=1}^{\infty} \cos(l\phi) \exp\left[-l^2 \frac{Dt}{R^2}\right] \right\}$$

This probability is normalised with respect to integration over a infinitesimal ring along the cylinder $Rd\phi$:

$$\begin{aligned} \int_0^{2\pi} p(\phi, t) R d\phi =& \int_0^{2\pi} \frac{1}{\pi R} \left\{ \frac{1}{2} + \sum_{l=1}^{\infty} \cos(l\phi) \exp\left[-l^2 \frac{Dt}{R^2}\right] \right\} R d\phi \\ =& \frac{1}{\pi} \left\{ \int_0^{2\pi} \frac{1}{2} d\phi + \sum_{l=1}^{\infty} \exp\left[-l^2 \frac{Dt}{R^2}\right] \int_0^{2\pi} \cos(l\phi) d\phi \right\} \\ =& \frac{1}{\pi} \left\{ \pi + \sum_{l=1}^{\infty} \exp\left[-l^2 \frac{Dt}{R^2}\right] \left[\frac{1}{l} \sin(2\pi l)\right] \right\} \\ =& 1 + \sum_{l=1}^{\infty} \exp\left[-l^2 \frac{Dt}{R^2}\right] \cdot 0 = 1 \end{aligned}$$

To find the MSD we first compute the squared distance between a point at our intial density configuration, $\mathbf{x}_0 = (R, 0, 0)$, and an arbitrary point $\mathbf{x} = (R\cos(\phi), R\sin(\phi), z^2)$:

$$r^2 = \|\mathbf{x}(\phi) - \mathbf{x}_0\|^2 = \left(R^2(\cos\phi - 1)^2 + R^2 \sin^2\phi + z^2\right) = 2R^2(\cos\phi - 1) + z^2$$

Now we can compute the mean squared displacement:

$$\begin{aligned} \left\langle \delta x^2 \right\rangle =& \left\langle r^2 \right\rangle = \left\langle 2R^2(1-\cos\phi) + z^2 \right\rangle \\ =& \int_0^{2\pi} \left(2R^2(1-\cos\phi) + z^2\right) \frac{1}{\pi R} \left\{ \frac{1}{2} + \sum_{l=1}^{\infty} \cos(l\phi) \exp\left[-l^2 \frac{Dt}{R^2}\right] \right\} R d\phi \\ =& \left\langle 2R^2 \right\rangle - \left\langle 2R^2 \cos\phi \right\rangle + \left\langle z^2 \right\rangle \end{aligned}$$

In this case the expectation values only deal with ϕ-dependence, so both $\left\langle 2R^2 \right\rangle$

and $\langle z^2 \rangle$ remain unchanged. This only leaves $\langle 2R^2 \cos\phi \rangle$ to be computed:

$$\begin{aligned}
\langle 2R^2 \cos\phi \rangle =& \frac{1}{\pi R} \int_0^{2\pi} 2R^2 \cos\phi \left\{ \frac{1}{2} + \sum_{l=1}^{\infty} \cos(l\phi) \exp\left[-l^2 \frac{Dt}{R^2}\right] \right\} R d\phi \\
=& \frac{2R^2}{\pi} \int_0^{2\pi} \frac{1}{2} \cos\phi d\phi + \sum_{l=1}^{\infty} \exp\left[-l^2 \frac{Dt}{R^2}\right] \int_0^{2\pi} \cos(l\phi) \cos\phi d\phi \\
=& \frac{2R^2}{\pi} \left[0 + \sum_{l=1}^{\infty} \exp\left[-l^2 \frac{Dt}{R^2}\right] \pi \delta_{l1} \right] = 2R^2 \exp\left[-\frac{Dt}{R^2}\right]
\end{aligned}$$

In the last step δ_{l1} is Kronecker's delta.

The diffusion along the z-direction is not affected by the cylinder, so we have $\langle z^2 \rangle = 2Dt$. Combining this with $\langle 2R^2(1 - \cos\phi) \rangle$ we find for the mean squared displacement that

$$\langle \delta x^2 \rangle = \langle z^2 \rangle + \langle 2R^2(1 - \cos\phi) \rangle = 2Dt + 2R^2 \left(1 - \exp\left[-Dt/R^2\right]\right) \quad (1)$$

In the limit of small t we have $\exp\left[-Dt/R^2\right] \approx 1 - Dt/R^2$ and equation (1) becomes $\langle \delta x^2 \rangle \approx 2Dt + 2R^2 \left(1 - 1 + Dt/R^2\right) = 4Dt$, the familiar expression for diffusion in a 2D plane.

2 Sphere

For the sphere we also need to solve the diffusion equation, but this time diffusion in all directions is hindered by the constraint. We therefore solve the diffusion equation in spherical coordinates $(x, y, z) = R(\cos\phi \sin\theta, \sin\phi \sin\theta, \cos\theta)$:

$$D \left[\frac{1}{R^2} \frac{\partial^2 n}{\partial \phi^2} + \frac{1}{R^2 \sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial n}{\partial \theta} \right) \right] = \frac{\partial n}{\partial t}$$

We can expand the left hand side in terms of spherical harmonics $Y_{lm}(\theta, \phi)$. Furthermore, if the initial density $n(\phi, \theta, t = 0)$ is located at the "north" pole, $n(\phi, \theta, t = 0) = n_0 \delta(\phi)\delta(\theta)/(\sin\theta R^2)$, then the problem is symmetry in ϕ and only the ϕ-independent spherical harmonics $Y_{l0}(\theta)$ contribute. For clarity, we use the definition

$$Y_{l0}(\theta) = \sqrt{\frac{2l+1}{4\pi}} P_l(\cos\theta),$$

with $P_l(x)$ Legendre polynomials. If we write $n(\phi, \theta, t) = A_l Y_{l0}(\theta) T(t)$ the diffusion equation reduces to an eigenvalue problem:

$$A_l D \frac{1}{R^2 \sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial Y_{l0}(\theta)}{\partial \theta} \right) T(t) = -l(l+1) \frac{D}{R^2} A_l Y_{l0}(\theta) T(t) = A_l Y_{l0}(\theta) T'(t)$$

This immediately reveals that $T(t) = T_0 \exp\left(-l(l+1)Dt/R^2\right)$, and we choose to absorb the factor T_0 into A_l, so we obtain

$$n(\theta, t) = \sum_{l=0}^{\infty} A_l Y_{l0}(\theta) \exp\left[-l(l+1) \frac{Dt}{R^2}\right] \quad (2)$$

This leaves us with the task of finding this coefficient A_l, which we do by integrating $n(\theta, t)$ multiplied by $Y_{l'0}(\theta)$ over the initial condition:

$$\begin{aligned}
&R^2 \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} n(\theta, t=0) Y_{l'0}(\theta) \sin\theta d\theta d\phi \\
=&R^2 \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} Y_{l'0}(\theta) \frac{n_0}{R^2 \sin\theta} \delta(\phi)\delta(\theta) \sin\theta d\theta d\phi = n_0 Y_{l'0}(0)
\end{aligned}$$

Integrating equation (2) in the same manner results in

$$\begin{aligned}
n_0 Y_{l'0}(0) =& R^2 \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} \sum_{l=0}^{\infty} A_l Y_{l0}(\theta) Y_{l'0}(\theta) \sin\theta d\theta d\phi \\
=& 2\pi R^2 \sum_{l=0}^{\infty} A_l \int_{\theta=0}^{\pi} Y_{l0}(\theta) Y_{l'0}(\theta) \sin\theta d\theta
\end{aligned}$$

In our convention for spherical harmonics, we have this becomes

$$\int_{\theta=0}^{\pi} Y_{l0}(\theta) Y_{l'0}(\theta) \sin\theta d\theta = \frac{\delta_{ll'}}{2\pi}$$

with $\delta_{ll'}$ again Kronecker's delta. Thus we find for the coefficients A_l that

$$n_0 Y_{l'0}(0) = 2\pi R^2 \sum_{l=0}^{\infty} A_l \frac{\delta_{ll'}}{2\pi} \rightarrow A_l = \frac{n_0 Y_{l0}(0)}{R^2}$$

Finally we use the definition for $Y_{l0}(\theta)$ to replace $Y_{l0}(\theta)$ with $\sqrt{(2l+1)/4\pi}$ to obtain

$$\begin{aligned}
n(\theta, t) =& \frac{n_0}{R^2} \sum_{l=0}^{\infty} \sqrt{\frac{2l+1}{4\pi}} Y_{l0}(\theta) \exp\left[-l(l+1)\frac{Dt}{R^2}\right] \\
=& \frac{n_0}{4\pi R^2} \sum_{l=0}^{\infty} (2l+1) P_l(\cos\theta) \exp\left[-l(l+1)\frac{Dt}{R^2}\right]
\end{aligned}$$

We can again divide this expression by n_0 to obtain the probability distribution of particles on the sphere:

$$p(\theta, t) = \frac{1}{4\pi R^2} \sum_{l=0}^{\infty} (2l+1) P_l(\cos\theta) \exp\left[-l(l+1)\frac{Dt}{R^2}\right] \tag{3}$$

In order to obtain a MSD from equation (3) we again compute the distance between a point in our initial distribution $\mathbf{x}_0 = R(0,0,1)$ and an arbitrary point $\mathbf{x} = R(\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$:

$$\begin{aligned}
\|\mathbf{x} - \mathbf{x}_0\|^2 =& R^2 \left(\sin^2\theta\cos^2\phi + \sin^2\theta\sin^2\phi + (1-\cos\theta)^2\right) \\
=& R^2(\sin^2\theta + 1 - 2\cos\theta + \cos^2\theta) = 2R^2(1-\cos\theta)
\end{aligned}$$

We now again calculate $\left\langle 2R^2(1-\cos\theta)\right\rangle$ using equation (3):

$$\begin{aligned}
\left\langle \delta x^2 \right\rangle =& \frac{1}{2\pi}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}(1-\cos\theta)\sum_{l=0}^{\infty}(2l+1)P_l(\cos\theta)e^{-l(l+1)Dt/R^2}R^2\sin\theta d\theta d\phi \\
=& \int_{\theta=0}^{\pi}(1-\cos\theta)\sum_{l=0}^{\infty}(2l+1)P_l(\cos\theta)\sin\theta\exp\left[-l(l+1)\frac{Dt}{R^2}\right]R^2 d\theta \\
=& R^2\sum_{l=0}^{\infty}(2l+1)\exp\left[-l(l+1)\frac{Dt}{R^2}\right]\int_{\theta=0}^{\pi}(1-\cos\theta)P_l(\cos\theta)\sin\theta d\theta
\end{aligned}$$

We know recognize in 1 and $\cos\theta$ the first two Legendre polynomials of $\cos\theta$: $P_0(\cos\theta) = 1$ and $P_1(\cos\theta) = \cos\theta$. Using the substitution $u = \cos\theta$ then simplifies the integral to

$$\int_{\theta=0}^{\pi}(1-\cos\theta)P_l(\cos\theta)\sin\theta d\theta = \int_{u=-1}^{1}(1-u)P_l(u)du = [2\delta_{l0}-\delta_{l1}]$$

We thus have for the MSD that

$$\begin{aligned}
\left\langle \delta x^2 \right\rangle =& R^2\sum_{l=0}^{\infty}(2l+1)\exp\left[-l(l+1)\frac{Dt}{R^2}\right]\left[2\delta_{l0}-\frac{2}{3}\delta_{l1}\right] = R^2\left[2-2e^{-2Dt/R^2}\right] \\
=& 2R^2\left[1-e^{-2Dt/R^2}\right] \qquad (4)
\end{aligned}$$