Coarse-graining from a hard sphere in a gas to Brownian motion with inertia

A hard sphere of radius R and mass M is immersed in an ideal gas at temperature T and number density ρ. Let m be the mass of each gas particles, with $m/M \ll 1$. The gas particles are distributed uniformly in space. Their momenta are given by the Maxwellian distribution

$$\eta(\mathbf{p}) = \frac{1}{\mathcal{N}} e^{-\beta p^2/2m} \tag{1}$$

with $\mathcal{N} = (2\pi m/\beta)^{3/2}$ and $\beta^{-1} = k_B T$. The mean speed of a gas particle is

$$\bar{v} = \sqrt{\frac{8}{m\pi\beta}} \tag{2}$$

Assume that the sphere starts with momentum $\mathbf{P}_0 = M\mathbf{V}_0$, where

$$V_0 \ll \bar{v} \qquad , \qquad \frac{1}{2}MV_0^2 \gg \frac{1}{2}m\bar{v}^2 \sim \beta^{-1} \tag{3}$$

i.e. the sphere moves far more slowly than a typical particle, but (due to its large mass) with much more kinetic energy. The sphere and gas particles interact via elastic collisions, each of which involves an exchange of energy between the sphere and gas particle. We expect the sphere to slow down, on average, as it evolves toward equipartition of energy, but many collisions must occur before the sphere loses a substantial fraction of its energy. Thus

$$t_0 \ll t_P \tag{4}$$

where t_0 is the average time between collisions, and t_P is a characteristic time scale over which the sphere's momentum decays.

In Problem 4 of Problem Set # 2, you showed that collisions with gas particles exert an average frictional force on the sphere, $\mathbf{F}_{fric} = -\gamma\mathbf{P}/M$, with friction coefficient

$$\gamma = \frac{4\pi}{3} R^2 m\bar{v}\rho \tag{5}$$

These considerations suggest that, at intermediate timescales between t_0 and t_P, we can model the evolution of the sphere's momentum by a Langevin equation in three dimensions:

$$\frac{d\mathbf{P}}{dt} = -\frac{\gamma}{M}\mathbf{P} + \boldsymbol{\xi} \tag{6a}$$

where the first term on the right gives the average force on the sphere, and the second represents random fluctuations around the average. We model the latter as isotropic, three-dimensional white noise:

$$\langle \boldsymbol{\xi} \rangle = \mathbf{0} \quad , \quad \langle \xi_i(t)\xi_j(t') \rangle = 2D_P\,\delta_{ij}\,\delta(t'-t) \tag{6b}$$

where the indices $i, j \in \{x, y, z\}$ label the three spatial axes. Eq. 6 is the Ornstein-Uhlenbeck process in the three degrees of freedom. The corresponding Fokker-Planck equation is

$$\frac{\partial f}{\partial t} = \frac{\gamma}{M} \boldsymbol{\nabla} \cdot (\mathbf{P} f) + D_P \nabla^2 f \tag{7}$$

where $f(\mathbf{P}, t)$ is the ensemble probability distribution in the momentum space of the sphere.

We have not yet computed the momentum diffusion coefficient D_P. To do so, we first note that

$$\frac{d}{dt}\langle P_i \rangle = -\frac{\gamma}{M}\langle P_i \rangle \quad , \quad \frac{d}{dt}\langle P_i P_j \rangle = -\frac{2\gamma}{M}\langle P_i P_j \rangle + 2D_P \delta_{ij} \tag{8}$$

These results are obtained by expressing the averages $\langle \cdot \rangle$ as integrals over $f(\mathbf{P}, t)$, then using Eq. 7 to evaluate their derivatives with respect to time, then integrating by parts and discarding boundary terms (details left as an exercise). From Eq. 8 we get

$$\frac{d\langle \mathbf{P} \rangle}{dt} = -\frac{\gamma}{M}\langle \mathbf{P} \rangle \quad , \quad \frac{d\sigma_P^2}{dt} = -\frac{2\gamma}{M}\sigma_P^2 + 6D_P \tag{9}$$

where $\sigma_P^2 \equiv \langle \mathbf{P} \cdot \mathbf{P} \rangle - \langle \mathbf{P} \rangle \cdot \langle \mathbf{P} \rangle$. For an initial a distribution $f(\mathbf{P}, 0) = \delta(\mathbf{P} - \mathbf{P}_0)$, Eq. 9 gives us the initial rate of growth of the momentum variance:

$$\left. \frac{d\sigma_P^2}{dt} \right|_{t=0} = 6D_P \tag{10}$$

Let us now calculate the left side of Eq. 10 from a microscopic, kinetic analysis.

Let Δt denote a time interval intermediate between t_0 and t_P. From $t = 0$ to $t = \Delta t$, the net change in the momentum of the sphere is given by

$$\Delta \mathbf{P} = \sum_k \delta \mathbf{P}_k \tag{11}$$

where $\delta \mathbf{P}_k$ is the change in its momentum during the k'th collision with a gas particle, and the sum is over all collisions in the interval $0 < t < \Delta t$. Because we have assumed an ideal gas, the values of $\delta \mathbf{P}_k$ are statistically independent, hence

$$\langle |\Delta \mathbf{P}|^2 \rangle = \left\langle \sum_k |\delta \mathbf{P}_k|^2 \right\rangle \tag{12}$$

For a given collision, let $\hat{\mathbf{n}}$ denote a unit vector pointing from the location of the collision to the center of the sphere, let $\mathbf{p}$ denote the momentum of the gas particle just before the collision, and let θ denote the angle between these vectors. Neglecting the recoil of the sphere, the net momentum imparted to the sphere is equal and opposite to the net change in the moment of the particle:

$$\delta\mathbf{P} = 2(\mathbf{p}\cdot\hat{\mathbf{n}})\,\hat{n} = 2p\cos\theta\,\hat{\mathbf{n}} \tag{13}$$

Let $\hat{\mathbf{n}}$ define the direction of the North Pole of polar coordinates, and θ the polar angle. Introducing ϕ as the azimuthal angle, the incoming momentum can be represented in polar coordinates $\mathbf{p} = (p, \theta, \phi)$, where $d^3p = p^2 \sin\theta\, dp\, d\theta\, d\phi$ gives the volume of an infinitesimal cell of momentum space. Now consider an infinitesimal surface element of area $d\sigma$ on the surface of the sphere. Then the rate of collisions occurring at the surface element $d\sigma$, with incoming momenta corresponding to the cell d^3p around $\mathbf{p}$, is:

$$\begin{aligned} \texttt{rate} &= \left[\rho\,\eta(\mathbf{p})d^3p\right]\,\frac{\mathbf{p}}{m}\cdot\hat{\mathbf{n}}\,d\sigma \\ &= \frac{\rho}{m\mathcal{N}}\,e^{-\beta p^2/2m}p^3\cos\theta\sin\theta\,dp\,d\theta\,d\phi\,d\sigma \end{aligned} \tag{14}$$

using Eq. 1. The quantity $\rho\,\eta(\mathbf{p})d^3p$ is the density of particles with incoming momenta in the designated cell, and $\mathbf{p}/m$ is the velocity of these particle; the product of these two is a current density. Combining Eqs. 12, 13 and 14 we get

$$\langle|\Delta\mathbf{P}|^2\rangle = \int_0^\infty dp \int_0^{\pi/2} d\theta \int_0^{2\pi} d\phi \int_\Omega d\sigma\,[\texttt{rate}]\,\Delta t\,\left(2p\cos\theta\right)^2 \tag{15}$$

where $\int_\Omega d\sigma$ denotes an integral over the surface of the sphere, which evaluates to $4\pi R^2$. The integral over the polar angle is from 0 to $\pi/2$, representing *incoming* particle momenta. Evaluating the above expression gives us

$$\langle|\Delta\mathbf{P}|^2\rangle = \frac{16\pi R^2\rho\Delta t}{m\mathcal{N}}\int_0^\infty dp\,p^5\,e^{-\beta p^2/2m}\int_0^{\pi/2} d\theta\cos^3\theta\sin\theta\int_0^{2\pi} d\phi \tag{16}$$

$$= \frac{16\pi R^2\rho\Delta t}{m\mathcal{N}}\left(\frac{2m}{\beta}\right)^3\left(\frac{1}{4}\right)(2\pi) = \frac{8m}{\beta}\pi R^2\rho\bar{v}\,\Delta t \tag{17}$$

Setting $\langle|\Delta\mathbf{P}|^2\rangle = 6D_P\Delta t$ (Eq. 10), we arrive at

$$D_P = \frac{1}{\beta}\frac{4\pi}{3}R^2\,m\bar{v}\rho \tag{18}$$

Comparing Eqs. 5 and 18 reveals that

$$\gamma = \beta D_P \tag{19}$$

which allows us to rewrite our Fokker-Planck equation (Eq. 7) as follows

$$\frac{\partial f}{\partial t} = D_P \boldsymbol{\nabla} \cdot \left[e^{-\beta P^2/2M} \boldsymbol{\nabla} \left(e^{\beta P^2/2M} f \right) \right] \tag{20}$$

We immediately see the Maxwellian distribution for the sphere,

$$\pi(\mathbf{P}) = \sqrt{\frac{\beta}{2\pi M}}\, e^{-\beta P^2/2M} \tag{21}$$

(compare with Eq. 1) is a stationary distribution of the Fokker-Planck equation. Thus the values of γ and D_P, calculated from the microscopic dynamics, guarantee that the equilibrium distribution $\pi(\mathbf{P})$ is a stationary solution of the Fokker-Planck equation obtained after coarse-graining (Eq. 20). This illustrates the idea that if we get the physics right at the microscopic level and we coarse-grain correctly, then the effective equation we obtain at the coarse-grained level will be thermodynamically consistent.

While Eq. 20 shows that the equilibrium state is a stationary solution of the Fokker-Planck equation, we have not yet shown that *all* initial distributions evolve toward that stationary solution. Substituting Eq. 19 into Eq. 8, upon inspection we see that asymptotically with time

$$\langle P_i \rangle \to 0 \quad , \quad \langle P_i P_j \rangle \to M\beta^{-1}\, \delta_{ij} \tag{22}$$

which are the values associated with $\pi(\mathbf{P})$ (Eq. 21). Using the generating function for the cumulants of momentum, $g(\boldsymbol{\lambda}) = \ln\langle e^{\boldsymbol{\lambda}\cdot\mathbf{P}}\rangle$, it is straightforward (but left as an exercise!) to obtain equations of motion for all the cumulants, analogous to Eq. 9. These equations reveal that, asymptotically with time, *all* momentum cumulants decay to zero, except the variance, σ_P^2. This shows that any initial distribution $f(\mathbf{P}, 0)$ decays to an isotropic Gaussian with mean zero and variance $3M\beta^{-1}$, that is to the Maxwellian distribution $\pi(\mathbf{P})$.

Eq. 6 represents three independent Ornstein-Uhlenbeck (OU) processes, for the components P_x, P_y and P_z. Using the explicit expression for the OU kernel (see Eq. 10 of the notes on the OU process, on the course website), it is straightforward to obtain

$$\langle P_i(s) P_j(s+t) \rangle = M\beta^{-1} e^{-\gamma|t|/M}\, \delta_{ij} \tag{23}$$

which gives the equilibrium correlation function between any two components of the momentum vector $\mathbf{P}$. Thus the sphere's momentum relaxes to equilibrium over a timescale

$$t_P = \frac{M}{\gamma} \tag{24}$$

Coarse-graining from Brownian motion with inertia to overdamped Brownian motion

Let us combine the coarse-grained equation of motion for the sphere's momentum, $\mathbf{P}$, with an equation of motion for its position, $\mathbf{R}$:

$$\frac{d\mathbf{R}}{dt} = \frac{\mathbf{P}}{M} \tag{25a}$$

$$\frac{d\mathbf{P}}{dt} = -\frac{\gamma}{M}\mathbf{P} + \boldsymbol{\xi} \tag{25b}$$

These lead to the following master equation for the probability distribution $f(\mathbf{R}, \mathbf{P}, t)$:

$$\frac{\partial f}{\partial t} = -\frac{\mathbf{P}}{M} \cdot \boldsymbol{\nabla}_{\mathbf{R}} f + D_P \boldsymbol{\nabla}_{\mathbf{P}} \cdot \left[e^{-\beta P^2/2M} \boldsymbol{\nabla}_{\mathbf{P}} \left(e^{\beta P^2/2M} f \right) \right] \tag{25c}$$

where $\boldsymbol{\nabla}_{\mathbf{R}} \equiv \partial/\partial_{\mathbf{R}}$ and $\boldsymbol{\nabla}_{\mathbf{P}} \equiv \partial/\partial_{\mathbf{P}}$.

Letting $\mathbf{P}(t)$ denote a solution of Eq. 25b for a given realization of the noise $\boldsymbol{\xi}(t)$, we have

$$\frac{d\mathbf{R}}{dt} = \frac{1}{M}\mathbf{P}(t) \tag{26}$$

where $\mathbf{P}(t)$ is a stationary random signal whose statistical properties are characterized by Eq. 23. Over timescales much longer than the momentum decay time t_P, this random signal can be replaced by white noise with the following statistics:

$$\langle P_i(s) P_j(s+t) \rangle = \frac{2M^2}{\beta\gamma}\, \delta_{ij}\, \delta(t) \tag{27}$$

where the factor $2M^2/\beta\gamma$ was determined by integrating Eq. 23 from $t = -\infty$ to $t = +\infty$.

The above equations can be rewritten conveniently as

$$\frac{d\mathbf{R}}{dt} = \mathbf{V}(t) \quad , \quad \langle V_i(s) V_j(s+t) \rangle = 2D\, \delta_{ij}\, \delta(t) \quad , \quad D = \frac{1}{\beta\gamma} \tag{28a}$$

which describes overdamped Brownian motion in three dimensions. An ensemble of trajectories evolving under Eq. 28a is described by a probability distribution $f(\mathbf{R}, t)$ governed by the diffusion equation

$$\frac{\partial f}{\partial t} = D \nabla^2 f \tag{28b}$$

with $\nabla^2 \equiv \nabla^2_{\mathbf{R}}$. Going from Eq. 25 to Eq. 28 represents one more step of coarse-graining, in which the sphere's momentum is eliminated. Note that this procedure gives us the correct Einstein-Smoluchowski relation between the diffusion and friction constants: $D = 1/\beta\gamma$.