Einstein's Fluctuation-Dissipation Relation [nln67]

Consider a colloid of volume V suspended in a fluid.
Excess mass: $m = V(\rho_{\text{coll}} - \rho_{\text{fluid}})$.
External (gravitational) force directed vertically down: $F_{\text{ext}} = -mg$.

Smoluchowski equation [nln66]:

$$\frac{\partial}{\partial t}n(z,t) = D\frac{\partial^2}{\partial z^2}n(z,t) + \gamma^{-1}\frac{\partial}{\partial z}\big[n(z,t)mg\big].$$

Stationary solution: $\partial n/\partial t = 0 \quad \Rightarrow \; n = n_{\text{s}}(z)$.

$$\Rightarrow \; \frac{d}{dz}\left[D\frac{dn_{\text{s}}}{dz} + \frac{mg}{\gamma}n_{\text{s}}\right] = 0; \quad n_{\text{s}}(\infty) = 0, \quad \left.\frac{dn_{\text{s}}}{dz}\right|_{z=\infty} = 0.$$

$$\Rightarrow \; n_{\text{s}}(z) = n_{\text{s}}(0)\exp\left(-\frac{mg}{\gamma D}\,z\right).$$

Comparison with law of atmospheres (thermal equilibrium state) [tex150],

$$n_{\text{eq}}(z) = n_{\text{eq}}(0)\exp\left(-\frac{mg}{k_{\text{B}}T}\,z\right),$$

implies

$$D = \frac{k_{\text{B}}T}{\gamma} \qquad \text{(Einstein relation)}.$$

This is an example of a relation between a quantity representing fluctuations (D) and a quantity representing dissipation (γ).

The Einstein relation was used to estimate Avogadro's number N_{A}:

- Colloid in the shape of a solid sphere of radius a.
- Motion in incompressible fluid with viscosity η.
- Stokes' law for drag force: $F_{\text{drag}} = -6\pi\eta a v = -\gamma v$.
- Damping constant $\gamma = 6\pi\eta a$ (experimentally accessible).
- Diffusion constant D (experimentally accessible).
- Ideal gas constant $R = N_{\text{A}}k_{\text{B}}$ (experimentally accessible).
- Avogadro's number: $N_{\text{A}} = \dfrac{RT}{6\pi\eta a D}$.