TD 9: Langevin Equation

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Consider the Langevin equation

$$\frac{\mathrm{d}\mathbf{v}}{\mathrm{d}t} = -\gamma \mathbf{v} + \frac{\mathbf{F}(t)}{m}, \tag{1}$$

where $\mathbf{v} = \frac{\mathrm{d}\mathbf{x}}{\mathrm{d}t} \in \mathbb{R}^3$ is the velocity of a particle of mass m, γ is the linear (Stokes) drag coefficient and $\mathbf{F}(t)$ a random force experienced by the particle. We assume that the random force is 0 on average $\overline{\mathbf{F}} = 0$, uncorrelated in time $\overline{\mathbf{F}(t_1) \cdot \mathbf{F}(t_2)} = 6Dm^2\delta(t_2 - t_1)$ and that $\overline{\mathbf{x}(t) \cdot \mathbf{F}(t)} = 0$, where the bar represents the ensemble average.

How to calculate the Avogadro number?

1. At thermal equilibrium, what is the average $\overline{\mathbf{v}^2}$?
2. Deduce that velocity and acceleration are not correlated in equilibrium, *i.e.* $\overline{\mathbf{v} \cdot \mathbf{a}} = 0$.
3. Show that at late times a particle in thermal equilibrium obeys

$$\overline{\mathbf{x}^2} = \frac{6k_BT}{m\gamma}t, \tag{2}$$

   where k_B is the Boltzmann constant and T the temperature.
4. How can you deduce experimentally the Avogadro number?

Analytic study of the Langevin equation. In this part, we solve explicitly the equation.

5. Prove that the explicit solution of Langevin equation for initial conditions $\mathbf{x}(t=0) = 0$ and $\mathbf{v}(t=0) = \mathbf{v}_0$ is

$$\mathbf{x}(t) = \frac{\mathbf{v}_0}{\gamma}\left(1 - e^{-\gamma t}\right) + \int_0^t dt' \int_0^{t'} dt'' \frac{\mathbf{F}(t'')}{m} e^{-\gamma(t'-t'')}. \tag{3}$$

6. Why is it reasonable to assume $\overline{\mathbf{x}(t) \cdot \mathbf{F}(t)} = 0$? Derive $\overline{\mathbf{x}(t_1) \cdot \mathbf{F}(t_2)}$ from the solution $\mathbf{x}(t)$ calculated in the previous question. When is $\overline{\mathbf{x}(t) \cdot \mathbf{F}(t)} = 0$ violated?
7. Compute $\sigma_x^2 = \overline{(\mathbf{x} - \overline{\mathbf{x}})^2}$ directly from the solution $\mathbf{x}(t)$ of the Langevin equation. What conclusion can we deduce.

Einstein relation. We link the diffusivity with the mobility and the drag.

8. The mobility μ is defined by $\overline{\mathbf{v}}_\infty = \mu \mathbf{F}_{ext}$, where $\mathbf{F}_{ext}$ is an applied external force and $\overline{\mathbf{v}}_\infty$ is the average velocity of the particle of mass m in the long-time limit. If we have a density ρ of molecules, what is the induced flux $\mathbf{j}_\mu$?
9. Additionally, when ρ is non-uniform there is a diffusive flux $\mathbf{j}_\rho = -D_x \nabla \rho$. Show that for a classical particle in a heat path at thermal equilibrium we get

$$D_x = \mu k_B T. \tag{4}$$

   This result is known as Einstein relation and is a special case of the more general fluctuation-dissipation theorem. It relates the diffusion constant to measurable observables of the system.
10. Explicit the links between γ and μ and between D and D_x. Deduce the the diffusivity for a particle in the context of a Stokes force.

Only when you have finished all the exercises

The Wikipedia Moment. JOSIAH WILLARD GIBBS (1839-1903).

Gibbs was born in New Haven, Connecticut. He belonged to an old Yankee family that had produced distinguished American clergymen and academics since the 17th century. Willard Gibbs was educated at the Hopkins School and entered Yale College in 1854 at the age of 15. At Yale, Gibbs received prizes for excellence in mathematics and Latin, and he graduated in 1858. He remained at Yale as a graduate student at the Sheffield Scientific School. In 1863, Gibbs received the first Doctorate of Philosophy (Ph.D.) in engineering granted in the US, for a thesis entitled ”On the Form of the Teeth of Wheels in Spur Gearing”, in which he used geometrical techniques to investigate the optimum design for gears. In 1861, Yale had become the first US university to offer a Ph.D. degree and Gibbs's was only the fifth Ph.D. granted in the US in any subject.

A few years later, Gibbs traveled to Europe with his sisters. They spent the winter of 1866-67 in Paris, where Gibbs attended lectures at the Sorbonne and the Coll de France, given by such distinguished mathematical scientists as Joseph Liouville and Michel Chasles. Moving to Berlin, Gibbs attended the lectures taught by mathematicians Karl Weierstraß and Leopold Kronecker, as well as by chemist Heinrich Gustav Magnus. In August 1867, Gibbs's sister Julia was married in Berlin to Addison Van Name, who had been Gibbs's classmate at Yale. The newly married couple returned to New Haven, leaving Gibbs and his sister Anna in Germany. In Heidelberg, Gibbs was exposed to the work of physicists Gustav Kirchhoff and Hermann von Helmholtz, and chemist Robert Bunsen. At the time, German academics were the leading authorities in the natural sciences, especially chemistry and thermodynamics.

Gibbs returned to Yale in June 1869 and briefly taught French to engineering students. It was probably also around this time that he worked on a new design for a steam-engine governor, his last significant investigation in mechanical engineering. In 1871, he was appointed Professor of Mathematical Physics at Yale, the first such professorship in the United States. Gibbs, who had independent means and had yet to publish anything, was assigned to teach graduate students exclusively.

Gibbs published his first work in 1873. His papers on the geometric representation of thermodynamic quantities appeared in the Transactions of the Connecticut Academy. These papers introduced the use of different type phase diagrams, which were his favorite aids to the imagination process when doing research, rather than the mechanical models, such as the ones that Maxwell used in constructing his electromagnetic theory, which might not completely represent their corresponding phenomena.

Gibbs then extended his thermodynamic analysis to multi-phase chemical systems (i.e., to systems composed of more than one form of matter) and considered a variety of concrete applications. He described that research in a monograph titled ”On the Equilibrium of Heterogeneous Substances”, published by the Connecticut Academy in two parts that appeared respectively in 1875 and 1878. That work, which covers about three hundred pages and contains exactly seven hundred numbered mathematical equations, begins with a quotation from Rudolf Clausius that expresses what would later be called the first and second laws of thermodynamics: ”The energy of the world is constant. The entropy of the world tends towards a maximum.” Gibbs's monograph rigorously and ingeniously applied his thermodynamic techniques to the interpretation of physico-chemical phenomena, explaining and relating what had previously been a mass of isolated facts and observations. The work has been described as ”the Principia of thermodynamics” and as a work of ”practically unlimited scope”.

Gibbs coined the term statistical mechanics and introduced key concepts in the corresponding mathematical description of physical systems, including the notions of chemical potential (1876), and statistical ensemble (1902). Gibbs's derivation of the laws of thermodynamics from the statistical properties of systems consisting of many particles was presented in his highly influential textbook Elementary Principles in Statistical Mechanics, published in 1902, a year before his death.

Gibbs died in New Haven on April 28, 1903, at the age of 64, the victim of an acute intestinal obstruction.