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RAPID COMMUNICATION

The rate of energy transfer from air as an initially stationary particle acquires Brownian motion

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Abstract
Physical simulation methods are used to determine the average time that is required for the molecules in standard air to transfer sufficient energy to an initially stationary particle to bring it to equilibrium with the gas as a Brownian particle. Individual particle trajectories are subject to random fluctuations and the average relaxation times are determined as ensemble averages over thousands of trajectories. The average initial power input to the particle is given by the equilibrium energy divided by the relaxation time. The relaxation time is determined for both spherical and cylindrical particles which vary in mass, diameter and, in the case of the cylinder, aspect ratio. The particle mass is normalized by the mass of an average air molecule, the diameter through the Knudsen number (the mean free path divided by the diameter) and the aspect ratio is the cylinder length to diameter. The relaxation time is found to be directly proportional to the product of the mass ratio and the square of the Knudsen number and inversely proportional to the aspect ratio. Empirical relations are developed for the relaxation times in each case. Should a cylindrical particle be fixed to a surface, it becomes a cantilevered nanowire that, if piezotronic, is capable of extracting energy. The relevance of the second law to this process is discussed together with speculations about the possibility of energy harvesting from nanodevices in air.

Introduction

The mainstream theory [1,2] of Brownian motion is concerned with the diffusion of the particles after they have come to equilibrium with the gas. This paper is concerned with the time that is required for an initially stationary particle to gain the energy associated with the equilibrium state. For a gas at temperature T, the equilibrium energy is $\zeta kT/2$ where k is the Boltzmann constant and ζ is the number of degrees of freedom of the particle.

The study employs the direct simulation Monte Carlo, or DSMC, method [3] which provides a physical model of the gas at the molecular level. Computer constraints generally limit

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the number of simulated molecules to the millions and, when applied to problems with typical dimensions of the order of a meter, each simulated molecule represents an extremely large number of real molecules. The fluctuations in the number of simulated molecules are then a computational artefact that limits the accuracy of the calculation. However, for applications to microscale or nanoscale problems, there may be a one-on-one correspondence of real and simulated molecules and it has been shown [4] that the fluctuations in the simulated gas then accurately model those in the real gas. The Boltzmann equation is the standard mathematical model for a gas at the molecular level, but this equation neglects fluctuations.

A particle executes Brownian motion in air when it is sufficiently small for there to be significant fluctuations in the forces that are applied to it by the air molecules. The fluctuations in the number N of molecules in a volume V is described by the Poisson distribution that becomes indistinguishable from a normal distribution for $N \gg 1$. The standard deviation of the fluctuations is therefore equal to the inverse square root of the number in the sample. The number of molecules in a cubic meter, or number density n, of any gas at standard temperature and pressure is equal to the Loschmidt number 2.6867805×10^{25} so that significant fluctuations occur only in very small volumes. The mean spacing between molecules is $n^{-1/3}$ or 3.3387 nm so that a cube with a side length of 3.3387 nm contains, on an average, just one molecule. There are also significant fluctuations in the average one-way number flux N, momentum flux $\dot{p}$, and translational energy flux $\dot{q}$ across a sufficiently small element of area in the gas. The elementary kinetic theory results for these averages in an equilibrium gas are, respectively,

$$\dot{N} = nc/4, \quad \dot{p} = \pi nmc^2/16, \quad \text{and} \quad \dot{q} = \pi nmc^3/16 \tag{1}$$

m is the mass of a molecule and c is the mean molecular speed

$$c = \sqrt{(8/\pi)kT/m}. \tag{2}$$

The mean mass of air molecules is 4.81×10^{-26} kg and the mean molecular speed at standard temperature is 446.7 m/s. The number flux in standard air is therefore extremely large at 3.0007×10^{27} m^{-2}/s but, at the nanoscale, is just three molecules per square nanometer per nanosecond. The substitution of Eq. (2) into Eq. (1) shows that the momentum flux is $nkT/2$ or half the pressure 101,278 Pa in the gas. Should the element be part of a solid surface, the other half is provided by the reflected molecules. The one-way translational energy flux is 22,621 kW/m^2. This is a strikingly large value and it may be compared with the energy flux of 17.4 kW/m^2 associated with a wind of 30 m/s ($\approx$ 15 knots) in standard air. However, should the element be a surface at the temperature of the air, the same energy is contained in the molecules that are reflected from the surface and there is no net heat transfer. Should the reflected molecules have a temperature one degree K less than the incident molecules at the gas temperature, the net heat transfer would be about 83 kW/m^2 which is 60 times larger than the solar heat flux. There is a temperature difference between incident and reflected molecules when there is a temperature gradient normal to a surface. This is of the order of the mean free path λ times the gradient. The hard sphere mean free path in standard air is 49 nm so that the required magnitude of the macroscopic temperature gradient for a one degree temperature difference would be more than a million degrees per meter. The temperature jump associated with commonly occurring macroscopic temperature gradients in standard air is a very small fraction of one degree. At the same time, the microscopic fluctuations are fractions of the large one-way momentum and energy fluxes.

The Brownian relaxation process increases the average translational energy of the particle to that of a molecule in the ambient gas. This is matched by a drop in the average energy of the reflected molecules but, because of their large number, the fall in gas temperature is extremely small. Energy is conserved and, while the energy of the particle continues to fluctuate, it is effectively just another molecule. The situation is more complex for flexible nanoscale particles attached to a surface. Consider particles comprised of the piezoelectric nanowires that are the subject of a recent review [5]. These wires are flexible and generate electricity when subjected to fluctuating deflections. The introduction of the review refers to existing MEMS transducers that have dimensions of hundreds of micrometers and kHz frequencies. These are much larger than the particle size in this Brownian relaxation study, but the text of the review refers to theoretical studies involving piezoelectric nanowires of 50 nm diameter and 600 nm in length. These are on the scale of the Brownian particles and, should the fluctuating forces cause any deflection that leads to the generation of electricity, there would be a violation of most statements of the second law of thermodynamics.

In fact, one of the many statements of the second law is that it is impossible to generate energy from the natural fluctuations in a gas. Suggestions to the contrary date back more than a century when Smoluchowski proposed [6] the Brownian ratchet. This involved mechanisms that were in common use in the large-scale mechanical devices of the era, but are impossible to fabricate at the distance and time scales at which fluctuations are significant. Nevertheless, a number of physicists have found it necessary to offer proofs that such a device would not work. These concentrate on the details of the mechanisms and it is hardly possible to extend them to a simple system such as the piezoelectric nanobeam. Much depends on whether the second law is a statement of the impossible or the improbable. This is an argument that dates back well over a century when the physicists who regarded the second law as immutable objected to the use of the molecular hypothesis in Boltzmann's statistical derivation of the law. The so-called "energists" lost that argument in the first decade of the twentieth century when molecules and atoms were shown to be real rather than hypothetical. If the second law is merely based on experience with and observations of macroscopic systems comprised of a myriad of molecules, it would not necessarily be valid at the nanoscale and the statement at the beginning of this paragraph could be incorrect.

The second law lends itself to hyperbole and discussions in the area are often accompanied by the following quotation from Eddington [7] "... the Second Law of Thermodynamics, holds ... the supreme position among the laws of Nature. If ... your theory is found to be against the second law of thermodynamics, I can give you no hope; there is nothing for it but to collapse in deepest humiliation." This assertion was made well after the statistical interpretation