Nano World Journal

http://dx.doi.org/10.17756/nwj.2017-040

Technical Note

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The Possibility of Harvesting Useful Energy from the Thermal Motion of Air Molecules

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Received: November 10, 2016
Accepted: February 03, 2017
Published: February 07, 2017

Citation: Bird GA. 2017. The Possibility of Harvesting Useful Energy from the Thermal Motion of Air Molecules. *NanoWorld J* 3(1): 18-22.

Published by United Scientific Group

Abstract

Direct simulation methods have been used to model the motion of initially stationary microscopic spheres following their release into the atmosphere. The spheres have diameters of the order of 10 nm and acquire energy from the slightly cooled air as they develop Brownian motion. While the individual trajectories vary wildly, an ensemble average over tens of thousands of trajectories yields a classical relaxation curve. The initial energy input from the air to a sphere is determined as a function of its diameter and mass. The energy flux to and from the fluctuations is also calculated along with the inward heat flux at the molecular level. The values of these quantities indicate that, while a sufficiently large number of sufficiently small devices might extract useful energy from air, the requirements with regard to size are beyond current nano-technology.

Keywords

Air, Energy source, Brownian, Relaxation

Introduction

Any suggestion that it might be possible harvest energy from air in order to do useful work that eventually returns that energy to the atmosphere would place the author at risk of suffering the fate predicted by Eddington [1] that "…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 is especially the case because the suggestion came to prominence more than a hundred years ago when Smoluchowski [2] proposed the Brownian ratchet and the intervening period has seen many papers that have presented arguments against the proposal. It has become so well known that the term "Brownian ratchet" is now applied [3] to any device that is driven by microscopic fluctuations even when it is unrelated to Brownian motion and does not involve a ratchet.

The haphazard motion of small particles that are suspended in a liquid was first observed by Brown in 1827. This motion was not understood until the early 20th century when the underlying theory and observations [4] not only led to the overdue acceptance of the atomic nature of matter, but provided estimates of the magnitudes of the molecular properties such as Avogadro's number. The realization that any macroscopic system contains an astronomical number of molecules also led to statistical interpretations of the second law. However, it is only at the start of the 21st century that the validity of second law has been seriously questioned [5, 6], especially for mesoscopic systems that contain only a few thousand molecules.

The conventional theory [7] of Brownian motion assumes thermal equilibrium between the particle and air and applies only to fully developed or equilibrium motion. It predicts that the average displacement of a particle from an arbitrarily chosen initial location is proportional to the square root of the elapsed time from the instant when the molecule was at that location. This means that the "diffusion velocity" is inversely proportional to the square root of the elapsed time. Note that the diffusion velocity relates to the trajectory of the particle and is distinct from the actual velocity which is sometimes called the ballistic velocity. The average values of both the diffusive and ballistic speeds are subject to fluctuation, but the mean value of the ballistic speed does not vary with time and may be regarded as a "steady" quantity. The dependence of the diffusion velocity on time often leads to confusion and it must be emphasised that the starting point for the elapsed time may be at any time after the establishment of fully developed Brownian motion.

A particle in a liquid is simultaneously influenced by a large number of atoms or molecules and the Brownian motion is a result of variations in the net force on the particle. Brownian motion also occurs in a gas but there is then a very short time interval between the successive molecule impacts and the particle executes a variable-step random walk in three-dimensional space. The characteristic distance at the molecular scale in a gas is the average distance that a molecule moves between intermolecular collisions. This mean free path in air at the standard temperature and pressure is 49 nm so that the average number of molecules in a cubic mean free path is 3,856. The ratio of the mean free path to the diameter of the particle is called the Knudsen number. A particle with a Knudsen number well above unity together with the adjacent air molecules that maintain its Brownian motion occupy less than a cubic mean free path and constitute a mesoscopic system.

A particle in fully established Brownian motion is in thermal equilibrium with the air and both the translational and rotational velocities have a Maxwellian distribution such that the mean energy in each degree of freedom is $\frac{1}{2}kT$, where k is the Boltzmann constant and T is the temperature. At each collision, either the air molecule does work on the particle or the particle does work on the molecule. The energy of the particle fluctuates and there may be a net increase or decrease over a period of time that is very large in comparison with the mean collision time. Experiments with micron-sized latex spheres in water have shown [8] that the intervals over which there is a net increase in particle energy can be as long as a few tenths of a second. While this has been claimed to be a violation of the second law, a similar decrease is equally likely and the average energy is constant.

A stationary particle has zero kinetic energy and, if it has temperature T and is suddenly immersed in air also at a temperature T, a finite time is required for particle to develop Brownian motion. As noted above, it gains an average of $\frac{1}{2}kT$ per degree of freedom and this energy comes from the nearby molecules that are cooled to a temperature slightly below T. This contradicts the Kelvin statement [9] of the second law that: "It is impossible, by means of inanimate material agency, to derive mechanical effort from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects". There is a net transfer of energy from the thermal motion of air to a particle only while it is not in equilibrium with the air. Should there be a process to transfer energy from the particle, it would not come to equilibrium and the energy transfer could be continuous. There are no such processes for a free and inert particle, but if piezoelectric nanowires [10] could be produced with diameters of a few nanometers rather than the microns of existing wires, continuous energy could almost certainly be produced. This statement is based on quantitative studies [11, 12] of the initiation of the Brownian motion of a spherical particle. These studies are described in Section II and permit the informed speculation in Section III about whether or not it will ever be possible to harvest useful energy from air.

Initiation of the Brownian Motion of a Spherical Particle

The development of Brownian motion by an initially stationary sphere is not amenable to mathematical analysis but, because it involves the interaction of the particle with a limited number of molecules, it is an ideal subject for a probabilistic simulation of the physics. A direct Monte Carlo simulation is particularly straightforward when the Knudsen number based on the sphere diameter is large in comparison with unity. There is then little likelihood that the molecules that are incident on the sphere have been affected by the reflected molecules and it is a called a "free-molecule" or "collisionless" flow. The trajectory of the sphere is calculated as it interacts with a representative set of incident molecules. The random impact points are generated with a probability that depends on the velocity of the sphere and the properties of the incident molecules are sampled from their known distributions in an equilibrium gas at temperature T. The initial study [11] assumed elastic collisions between the air molecules and the particle, while the second employed the more realistic diffuse model for the gas-surface interaction. Diffuse reflection is inelastic in that the sum of the molecule and particle energies is not conserved. There is, therefore, heat transfer to or from the particle at each collision and its temperature fluctuates. Also, diffuse reflection exerts a shear stress as well as a normal force, or pressure, on the particle so that it develops a fluctuating rotational as well as translational velocity. There are three rotational degrees of freedom in addition to the three translational degrees of freedom so that the average translational and rotational energies are equal

A stationary sphere of given mass and diameter was exposed at zero time to air at standard temperature and pressure and was then subjected to representative molecular collisions. Most calculations were made for a sphere with a Knudsen number Kn=10 and a specific weight equal to that of water. The sphere in this "reference case" has a diameter of 4.9 nm and a mass of 6.16×10^{-23} kg, while an average air molecule has an effective diameter of 0.415 nm and a mass of 4.81×10^{-26} kg. The mass ratio $\tilde{M}$ is defined as the ratio of the particle mass to the average molecular mass and is equal to 1281. A large number of independent trajectories were calculated and there were very large variations in the history of the particle

energies. The particle is subject to an average of 264 molecular impacts per nanosecond and the colored lines in Figure 1 shows the translational energy of a 10 typical particles over the first 20 ns. The particle energy is divided by (3/2) *k* so that it is expressed as degrees Kelvin. It should be emphasised that this is the "temperature" that corresponds to the kinetic energy and is unrelated to the actual temperature of the particle. This is assumed to be uniform and equal to the air temperature of 273 K at zero time and, because energy is not conserved in an inelastic collision, it fluctuates by a few degrees during the subsequent motion.

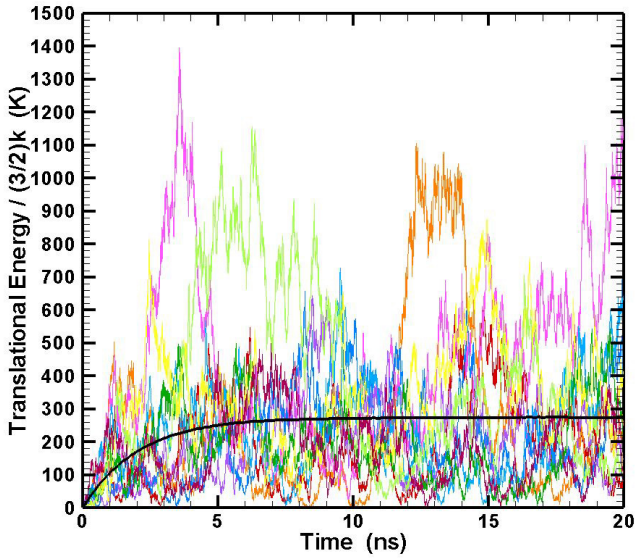

Figure 1: Ten typical particle energy histories together with the mean of 100,000 histories.

The wide spread in the particle energies at any instant is evident in Figure 1. An ensemble average must be made over tens of thousands of particles before the fluctuations cease to be noticeable. The black line in Figure 1 is the average of 100,000 particle trajectories and exactly fits a classical exponential relaxation curve leading to the uniform 273 K that is expected from equipartition. The relaxation time τ based on the initial slope of this curve is 2.1 ns and the mean initial power input $\bar{P}$ from the gas to the particle is given by the equilibrium energy divided by this time, or 0.0086 nW. Other cases were calculated and the results fit the empirical equation

$$\bar{P} = 940\left(1+1/\tilde{R}\right)^2 \Big/ \left(\tilde{M}K_n^2\right) \quad \ldots\ldots\ldots (1)$$

where $\tilde{R}$ is the ratio of the particle diameter to the effective molecular diameter.

The moment of inertia of the particle assumes a solid sphere and the relaxation time for rotational energy was slightly faster than that for translational energy. The moment of inertia for a hollow sphere is larger by a factor of 5/3 and, for the same mass, the relaxation time increases by the same factor.

The particle energy *E* increases when the air does work on the particle and decreases when the particle does work on the air. The energy gain or loss may be sampled at each collision and the power imparted to the particle by the fluctuations is given by summing over the collisions that involve an energy increase and dividing by the time over which the summation is made. The average power imparted to the particle is

$$\bar{P} = \sum \Delta E_{+ve} / \Delta t \quad \ldots\ldots\ldots\ldots\ldots (2)$$

and a similar sum over the negative energy changes determines average power imparted by the particle to the air. Note that the sum of the energy transfers is proportional to time so that the result is independent of Δt. While the choice of time step is arbitrary, it affects only the sampling interval between the data points. Figure 2 shows the value from an average of 100,000 particle trajectories for the reference case and this demonstrates that the air does more work on the particle than the particle does work on the air during the establishment of the motion.

For the reference case, the mean rate of energy transfer to and from the fluctuations is about seven times the mean initial power imparted to the particle. The empirical result for the energy flux in nanoWatts from calculations with a range of particle sizes and masses is

$$\bar{P} = 180\left(1+1/\tilde{R}\right)^2 \Big/ \left(\tilde{M}^{1/2}K_n^2\right) \quad \ldots\ldots\ldots\ldots\ldots (3)$$

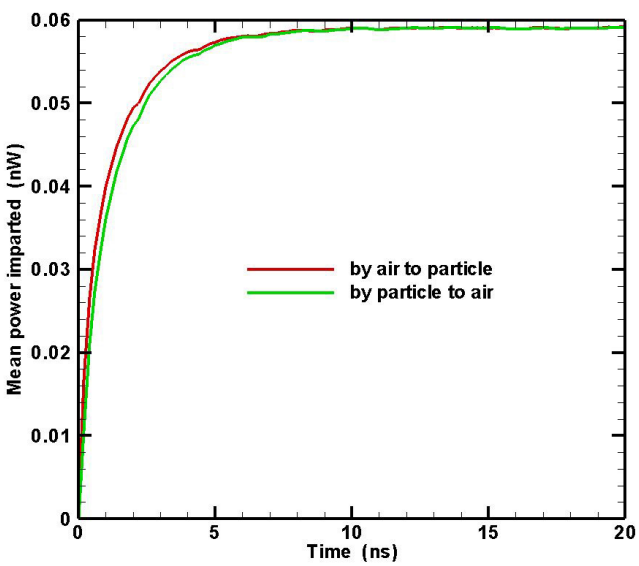

Figure 2: The mean rate of energy transfer to and from an initially stationary particle.

Molecular Fluxes at the Nanoscale

The number density of molecules in air at standard temperature and pressure is $n = 2.68678\times10^{25}$ /m³. This is a very large number but the average molecular mass m is similarly small at 0.481×10^{-24} kg so the density $\rho = nm = 1.29$ kg/m³ is of order unity. Standard kinetic theory results for the fluxes of number, momentum and energy that are incident to a surface element are, respectively,

$$\dot{N} = nc/4, \quad p_i = (\pi/16)nmc^2, \quad \text{and} \quad q_i = (\pi/16)nmc^3, \quad \ldots\ldots (4)$$

where

$$c = \sqrt{(8/\pi)kT/m} \quad \text{..... (5)}$$

is the average molecular speed, a molecule in equilibrium air at standard temperature moves with an average speed of 447 m/s between collisions with other molecule that occur with a frequency such that the mean free path λ is approximately 49 nm. Note that this motion is only at the nanoscale and the macroscopic velocities that appear in the continuum formulations such as the Navier-Stokes equations are zero. The macroscopic density has already been defined in terms of the molecular properties and the combination of equation 4 into equation 5 shows that the momentum flux due to the incident molecules is $p_i = \frac{1}{2}nkT$, or half the macroscopic pressure. The molecules that are reflected from the surface move in the opposite direction and supply the other half of the macroscopic pressure which is 101,278 N/m^2 at STP. This is a large number because the expression for p_i contains the square of the near sonic average molecular speed. The incident heat flux q_i is proportional to this velocity cubed and has the extremely large value of 22.61 MW/m^2. However, if the surface is at the same temperature as the gas, the energy flux of reflected molecules the same and the net heat flux is zero. Any net heat flux to or from a surface is entirely due to a temperature gradient normal to the surface. The coefficient of heat conduction of air is such that the macroscopic heat flux is only 0.0243 W/m^2 for a temperature gradient of one degree K per meter. The macroscopic and molecular fluxes are similar and this macroscopic gradient requires a temperature slip at the surface of 273 x 0.0243/22,610,000 or only 2.93 x 10^{-7} K.

The only consequence at the macroscopic level of the extremely high one-way heat flux at the molecular level is that it justifies the conventional assumption of zero temperature slip at a surface. However, it is the reason for the interest in air as a potential energy source at the nanoscale. The heat flux of 22.61 MW/m^2 is about twenty thousand times the maximum solar heat flux at the surface of the earth and there is an even larger factor with regard to the maximum usable energy flux associated with wind. Figure 2 shows that, during the time that an ensemble-averaged Brownian particle extracts energy from air, the average energy flux of the molecules incident on its surface is larger than the average energy flux carried away by the reflected molecules.

The average energy flux to and from the fully established or equilibrium fluctuations may be compared with the incident energy flux q_i to the surface. The surface area of a sphere with 4.9 nm diameter is 7.543 x 10^{-17} m^2 and the energy flux to the surface 1.705 nW. Figure 2 shows that the flux to and from the equilibrium Brownian motion of the sphere is only 3% of the incident energy flux to its surface, the effect of sphere diameter on this ratio is probably the best indicator of the required size of any object or device that could harvest energy from air. For a particle of given density, the diameter enters both the mass ratio and Knudsen number so that, ignoring the factor based on the radius ratio, the energy flux in equation 3 is proportional to the square root of the diameter. However, the surface area is proportional to the square of the diameter so that the energy flux decreases as the $\frac{3}{2}$ power of the diameter. Also, if it was possible to harvest energy from a device of the size of the sphere, the energy would be minute and useful energy could only come from a vast number of devices fabricated similarly to a semiconductor chip. The number of devices would be inversely proportional to the diameter so that the energy output per unit area would decline as the $\frac{7}{2}$ power of the diameter. equation 3 relates to the equilibrium or fully established rate of energy transfer, while equation 1 for the initial power to a stationary sphere relates to the nonequilibrium rate. This equation has the mass rather than the square root of the mass in the denominator so that, instead if the energy flux increasing as the square root of the diameter, it is inversely proportional to the diameter. The energy output per unit area in the nonequilibrium case decreases as the fifth power of the diameter.

It is unlikely than any energy harvesting device could be smaller than the 5 nm diameter of the sphere in the reference case. This is about ten times larger than an average air molecule and the device would be comprised of about a thousand atoms. Should the device be a flexible piezoelectric nanowire, the length could be much larger than the diameter, but the power output would be unlikely to exceed 0.01 nw. Useful power would require an enormously large number of such devices with sufficient spacing to prevent interference between adjacent wires. For example, if the 5 nm diameter wires were spaced at 100 nm, there would be 10^{14} wires per square meter and the power output would be one KW/m^2.

Conclusions

The initiation of the Brownian motion of microscopic particles demonstrates that, despite some interpretations of the Second Law, energy can be extracted from air at the nanoscale. Direct simulation studies have determined the magnitude of the rates of energy transfer that are involved in this process for a sphere and show that they decrease strongly with the diameter of the sphere. The energy imparted to the motion an inert object is not a useful source of energy, but energy could similarly be transferred to a flexible piezoelectric nanowire if it was possible to fabricate a sufficiently small wire. Speculative calculations indicate that useful energy could be harvested if a surface was covered by a sufficiently large number of nanowires. This is beyond current technology and may never be feasible. At the same time, the future might see nano-devices that are unrelated to nanowires but can more effectively take advantage of the enormous one-way molecular energy flux of more than 22 Mega Watts per square meter in equilibrium air at standard temperature and pressure. For power to be generated by a nano-device, the energy imparted by the incident molecules must be larger than the energy carried away by the reflected molecules. There must be very few intermolecular collisions in the vicinity of the device in order to preserve the consequent nonequilibrium velocity distribution function. This is most easily achieved if the device is smaller than the mean free path and the spacing between devices is larger than the mean free path. Nanofabrication is a burgeoning field and it is important that there should be an awareness of the potential to harvest energy from air.

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