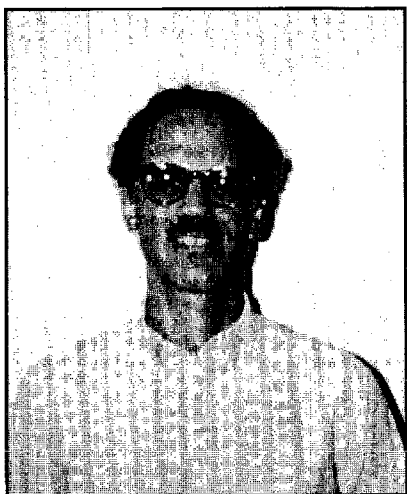


Thank You, Boltzmann, That Your Constant Is So Small

By Jeffrey J. Prentis



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Boltzmann's constant, $k = 1.38 \times 10^{-23}$ J/K, is the universal constant of nature that characterizes thermodynamic phenomena. In a world where this constant is large, such as $k = 1.38 \times 10^{-2}$ J/K, the behavior of nature would be highly unnatural, unpredictable, and unhealthy. In such a world, the following phenomena would be everyday occurrences: people levitating, objects jumping off tables, water flowing uphill, spontaneous combustion, glaciers melting, geysers freezing, blood boiling, chairs becoming too hot to sit on, oil and water mixing, sugar cubes reforming in tea, ice cubes forming in hot water, and lakes freezing in summer and boiling in winter. Perpetual motion machines (cars, planes, and ships) that extract energy from the earth, air, and sea would be commonplace.

This bizarre thermodynamic world (large k) complements the strange relativistic (small c) and quantum (large h) worlds of Mr. C.G.H. Tompkins.¹ The world inhabited by Mr. Tompkins obeys the same laws of physics as ours, but has different numerical values for the constants (such as $c = 1$ m/s and $h = 1$ Js), thereby greatly amplifying the effects of relativity and quantum mechanics.² Pondering such a world can be an effective tool to help understand the abstract and anti-intuitive ideas of physics.

In recent years, physics teachers have realized the need to incorporate more statistical physics into the introductory physics course.³ Several recent introductory physics textbooks include a special section on the statistical meaning of entropy.⁴

In this article, I show how a minimal set of basic ideas of statistical physics can be integrated into introductory thermodynamics and used to calculate the probability of thermodynamic states. We will imagine a world where Boltzmann's constant is $k = 1.38 \times 10^{-2}$ J/K and analyze the consequences quantitatively. In this world, the statistical nature of thermodynamics is exaggerated and becomes an integral part of everyday life. Students gain insight into the meaning of entropy and appreciate how natural (and paranormal) phenomena are governed by the laws of chance.

Basic Statistical Physics

In an introductory physics course, entropy is defined by the relation

$$\Delta S = \int \frac{dQ}{T} \quad (1)$$

This equation gives the change in entropy between any two thermodynamic states. The infinitesimal quantity of heat, dQ , refers to a reversible process and is not an exact differential. The student's knowledge of entropy is usually confined to this thermodynamic notion of entropy as "heat over temperature."

The microscopic meaning of entropy and the probabilistic nature of thermodynamic states is contained in the basic equations

$$S = k \ln \Omega \quad (2)$$

$$P \propto \Omega \quad (3)$$

Equation (2) is the microscopic meaning of entropy. In this celebrated equation, due to Ludwig Boltzmann, k is Boltzmann's constant and Ω is the thermodynamic probability. The thermodynamic probability (statistical weight) of a macroscopic state is defined as the number of microscopic states compatible with the macroscopic state.^{3,4} The microscopic state (or microstate) characterizes the small-scale dynamical behavior of each particle in the system, such as the position and velocity of each particle. The macroscopic state (or macrostate) characterizes the large-scale, bulk, thermodynamic behavior of the system, such as the temperature and pressure of the system. Equation (2) provides the fundamental connection between the microscopic (Ω) and the macroscopic (S) worlds. Equation (3) is the fundamental postulate of statistical mechanics.⁵ In words, this statistical postulate states: For an isolated system in equilibrium, each accessible microstate is equally probable. Hence, the statistical probability (P) is proportional to the thermodynamic probability (Ω). More specifically, the probability of finding a system in a particular macrostate is proportional to the number of microstates associated with the macrostate. Note that P is a fraction between zero and one, while Ω is a whole number typically much larger than one. It should also be noted that Eq. (1) refers to a thermodynamic process, whereas Eq. (3) refers to an equilibrium fluctuation. Equations (2) and (3) embody the statistical essence of the second law of thermodynamics. More specifically, $P \propto \exp(S/k)$, and hence the most probable macrostate is the macrostate for which S is maximum.

To illustrate the meaning of Ω and P , consider a simple toy system consisting of three fair coins. Each coin can exist in two microstates: heads (h) or tails (t). The system of three coins can exist in eight microstates. A macrostate is defined by the number of heads, denoted H . There are four macrostates: $H = 0, 1, 2, 3$. Consider the macrostate $H = 2$. There are three microstates (hht, hth, thh) associated with this macrostate. Thus the thermodynamic probability $\Omega(H)$ and the statistical probability $P(H)$ of the macrostate $H = 2$ are $\Omega(2) = 3$ and $P(2) = 3/8$. For real systems in nature, finding Ω and P is a much more difficult chore. One must use mechanics to find the microstates and statistics to count the microstates, i.e., statistical mechanics. The presentation in this article

avoids such complexity. Using Eq. (2), we can count microstates indirectly from a knowledge of the thermodynamic entropy via the relation $\Omega = e^{S/k}$.

The following warm-up exercise illustrates how to enliven the standard thermodynamics presentation by applying these basic physical statistics ideas to a real system in nature. Consider the prototype thermal process whereby two objects, each of heat capacity C , are placed in thermal contact. Initially, one object is "hot" at a temperature $T + \Delta T$ and the other object is "cold" at a temperature $T - \Delta T$. The final equilibrium temperature of both objects is T . The change in entropy of the isolated system during this thermal process, according to Eq. (1), is a standard thermodynamic calculation in introductory physics.⁶ To compute this entropy change, we imagine a reversible process whereby heat energy ($dQ = CdT$) is slowly removed from the hot object (so that its temperature decreases from $T + \Delta T$ to T) and slowly added to the cold object (so that its temperature increases from $T - \Delta T$ to T). The entropy change of the combined system is $\Delta S = \Delta S_h + \Delta S_c$, where the entropy change of the hot (h) object is

$$\Delta S_h = \int_{T+\Delta T}^T \frac{CdT}{T} \quad (4)$$

and the entropy change of the cold (c) object is

$$\Delta S_c = \int_{T-\Delta T}^T \frac{CdT}{T} \quad (5)$$

Assuming that C is a constant, these entropy integrals can be performed, using $\int dx/x = \ln x$, and then added to give

$$\Delta S = C \ln \left(\frac{T}{T+\Delta T} \right) + C \ln \left(\frac{T}{T-\Delta T} \right) \quad (6)$$

The hot and cold terms can be combined using $\ln x + \ln y = \ln(xy)$. Thus the change in entropy for this thermal process is

$$\Delta S = C \ln \left(\frac{T^2}{T^2 - \Delta T^2} \right) \quad (7)$$

This thermodynamic calculation of an entropy change typifies a student's exposure to entropy in introductory physics. Students learn how to compute entropy changes for natural processes, but they do nothing with the actual results except to note that ΔS is always a positive number or zero. The actual value of ΔS has little, if any, meaning. The macroscopic meaning of ΔS , in terms of heat-over-temperature, remains rather abstruse. It would be nice to more fully utilize the information contained in ΔS to gain insight into the microscopic meaning of entropy and the statistical nature

of thermodynamic equilibrium. Indeed, as we will show, the standard calculations and results for ΔS , that students encounter in the domain of pure thermodynamics, can be put to good use and naturally extended into the statistical realm of possibilities.

For example, one interesting question is: What is the probability for the objects to spontaneously become hot and cold once again? To answer this question, let $P(\Delta T)$ denote the probability for such an equilibrium fluctuation to occur where one object is at temperature $T + \Delta T$ and the other object is at $T - \Delta T$. From Eqs. (2) and (3), this statistical probability is related to the entropy change according to

$$\frac{P(\Delta T)}{P(0)} = e^{-\Delta S/k} \quad (8)$$

Note that $P(0)$ is the maximum probability corresponding to the most probable state ($\Delta T = 0$). Also note that a fluctuation in temperature corresponds to a fluctuation in the energy distribution between the two systems. Substituting the thermodynamic entropy change, Eq. (7), into the statistical probability ratio, Eq. (8), gives

$$\frac{P(\Delta T)}{P(0)} = \exp \left[-\frac{C}{k} \ln \left(\frac{T^2}{T^2 - \Delta T^2} \right) \right] \quad (9)$$

Using $a \ln x = \ln(x^a)$ and $\exp(\ln x) = x$, this probability expression simplifies to

$$\frac{P(\Delta T)}{P(0)} = \left(\frac{T^2}{T^2 - \Delta T^2} \right)^{-C/k} \quad (10)$$

Thus the probability for an isolated system to spontaneously become half hot ($T + \Delta T$) and half cold ($T - \Delta T$) is determined by

$$\frac{P(\Delta T)}{P(0)} = \left[1 - \left(\frac{\Delta T}{T} \right)^2 \right]^{C/k} \quad (11)$$

Note that this statistical probability depends on two dimensionless variables, $\Delta T/T$ and C/k . The heat capacity depends on the type of matter that the system is made of and the amount of matter. For example, for a monatomic gas, $C = (3/2)nR$ (at constant volume), while for a classical solid, $C = 3nR$, where n is the number of moles of matter and $R = 8.31$ J/Kmole is the universal gas constant.⁷ Hence, for solid objects, the probability for a temperature fluctuation in Eq. (11) assumes the more specialized form

$$\frac{P(\Delta T)}{P(0)} = \left[1 - \left(\frac{\Delta T}{T} \right)^2 \right]^{3nR/k} \quad (12)$$

Let's try some numbers. Consider one mole of a solid with heat capacity $C = 3nR = 25$ J/K. Note that $C \gg k$. For a fractional temperature change of $\Delta T/T = 0.10$, the relative

probability $P(\Delta T)/P(0)$ is equal to 0.99 raised to the power 1.8×10^{24} , which is a fantastically small number. This number can be expressed as $\exp(-1.8 \times 10^{22})$. Note that this small number can be interpreted as the reduction factor by which the number of accessible microstates decreases due to a 10% fluctuation from the most probable temperature: $\Omega(\Delta T) = \exp(-1.8 \times 10^{22})\Omega(0)$. In general, from Eq. (11), we can see that fluctuations will be significant only in the radically extreme cases where $\Delta T \ll T$ and/or $C \approx k$.

The fundamental equation that incorporates both of the physical statistics ideas presented in Eqs. (2) and (3) is

$$\frac{P(x)}{P(0)} = e^{-[S(0) - S(x)]/k} \quad (13)$$

where x is any value of a fluctuating macroscopic property of an isolated system in equilibrium, and $x = 0$ is the most probable value. This powerful relation allows us to calculate a statistical probability ratio from a thermodynamic entropy change. In other words, it allows us to quantitatively study the deviations away from the most probable state. Note that $\Delta S/k$ is the vital dimensionless ratio that determines the probability of the fluctuation. Boltzmann's constant (k) is the "entropy constant" that sets the natural scale for the exponential decay of the probability of the fluctuation as a function of the entropy change (ΔS) associated with the fluctuation. If $\Delta S = k$, then $P(x) = (1/e)P(0)$. If $\Delta S \ll k$, then $P(x) \approx P(0)$. If $\Delta S \gg k$, then $P(x) \approx 0$. Note that measurable fluctuations are extremely rare since $\Delta S \gg k$ for such fluctuations. Highly probable fluctuations are not observable since they have exceedingly small entropy changes, ΔS , on the order of k .

The basic ideas of statistical physics, represented in Eq. (13), will now be applied to a mechanical and a diffusive phenomenon: levitation of bodies in gravity and formation of holes in air.

Levitation

Levitation is the phenomenon whereby a body spontaneously elevates itself in the Earth's gravitational field. A scientific explanation of this process is that the levitator converts a small amount of the internal energy of the environment (Earth and/or air) into the mechanical energy needed for levitation. The Earth/air system serves as a vast reservoir of energy randomly distributed over its molecular constituents. Consider a body of mass m levitating at a height h in an environment of temperature T where the gravitational field strength is g (see Fig. 1). In this system, the macroscopic property of interest is the vertical height h of the mass above the ground. The most probable value is $h = 0$. There is nothing in the laws of physics (conservation of energy and the fundamental postulate) that prevents h from being nonzero. For this isolated system in equilibrium, h can assume all possible values between zero and infinity. It is important to realize that the levitation states ($h > 0$) are accessible states that can occur

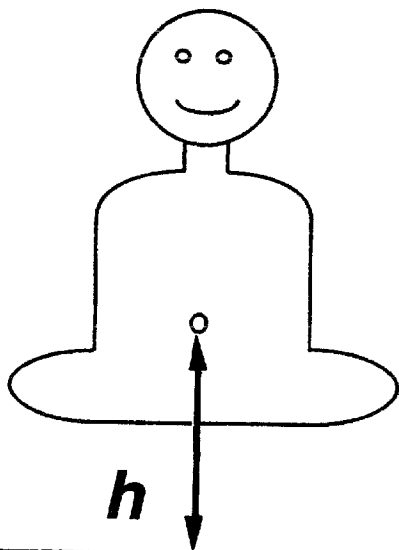


Fig. 1. A body levitating at a height h above the ground.

with a finite (albeit small) probability. The probability to levitate is not exactly zero.

Let $P(h)$ denote the probability to observe a body levitating a height h above the ground. According to the general Eq. (13), $P(h)$ is determined by

$$\frac{P(h)}{P(0)} = e^{-[S(0) - S(h)]/k} \quad (14)$$

Note that $h = 0$ is the most probable state for which $S(h)$ and $P(h)$ are maximum. The change in entropy, $S(0) - S(h)$, can be calculated using the thermodynamic definition:

$$S(0) - S(h) = \int_h^0 \frac{dQ}{T} \quad (15)$$

Computing this entropy change requires us to imagine a reversible process from h to 0. Note that the direction of the process has been chosen so that the initial state is h and the final state is 0. This choice is arbitrary since entropy is a state function whose difference only depends on the endpoints of the path. Such a choice corresponds to the more natural thermodynamic process whereby removing a constraint (a support) allows a mass to fall to the ground.

In the calculation of the entropy change, the body, the air, and the Earth are considered an isolated system at the same temperature T . During the process from h to 0, the internal energy of the system increases as the mechanical (gravitational potential) energy of the center of mass, mgh , is ultimately transformed into internal (thermal) energy. This change is the same as if an amount of heat $Q = mgh$ is reversibly added to the system at constant temperature T . Hence the change in entropy of the system is

$$S(0) - S(h) = \frac{mgh}{T} \quad (16)$$

Combining Eqs. (14) and (16) gives the levitation probability. Thus the probability $P(h)$ for a mass m to levitate a height h in an environment of gravity g and temperature T is determined by

$$\frac{P(h)}{P(0)} = e^{-mgh/kT} \quad (17)$$

Hence the probability for a 50-kg person to levitate 1 cm above the ground in a 300-K environment is $P(1 \text{ cm}) = \exp(-1.2 \times 10^{21}) P(0)$. Levitation is highly probable only if $mgh \approx kT$. This means that a person can easily levitate at heights on the order of 10^{-23} m or smaller, such as the Planck length! In general, since macroscopic mechanical energies are much larger than thermal energies ($mgh \gg kT$), the most probable state ($h = 0$) is the "only" state.

If the levitating body is an oxygen molecule, then Eq. (17) gives the well-known law of atmospheres⁸ that describes the exponential decrease in air density or air pressure with altitude. In particular, the probability to find an oxygen molecule "levitating" at 1 km above sea level in a 280-K atmosphere is $P(1 \text{ km}) = 0.87 P(0)$. This provides a wonderful interpretation of the atmosphere as a system of spontaneously levitating air molecules!

In a world where $k = 1.38 \times 10^{-2}$ J/K, levitation of macroscopic objects is the norm.⁹ If $T = 300$ K, and $m = 50$ kg, then Eq. (17) becomes $P(h) = \exp(-1.2h) P(0)$, where h is in centimeters. Hence the probability for a 50-kg person to levitate 1 cm above the ground is $P(1 \text{ cm}) = 0.30 P(0)$. The time spent 1 cm above the ground is approximately one-third the time spent on the ground. People and other bodies would form an atmosphere!¹⁰

Hole in the Air

Consider the phenomenon whereby a vacuum spontaneously forms in a region of the air. To form this "hole" in the air, the air molecules in the hole region must suddenly conspire to move out of the region en masse.

Let $P(v)$ denote the probability that a hole of volume v is spontaneously formed in the air. The air is contained in an isolated room of volume V (see Fig. 2). According to the general Eq. (13), $P(v)$ is determined by

$$\frac{P(v)}{P(0)} = e^{-[S(0) - S(v)]/k} \quad (18)$$

Note that $v = 0$ is the most probable state for which $P(v)$ and $S(v)$ are maximum. It corresponds to the air molecules uniformly filling the entire volume of the room.

The change in entropy is

$$S(0) - S(v) = \int_v^0 \frac{dQ}{T} \quad (19)$$

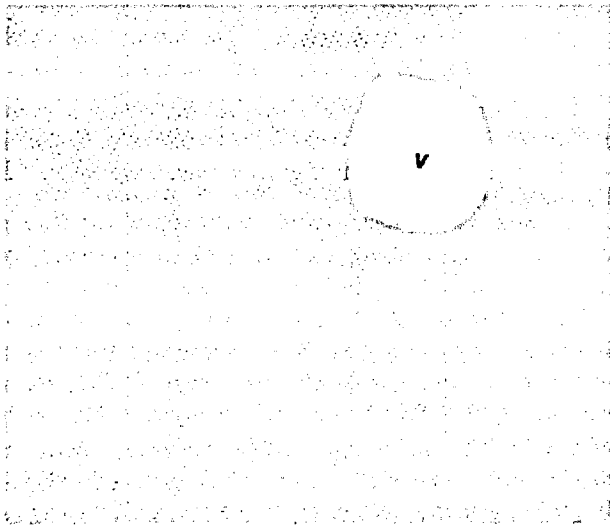


Fig. 2. A hole of volume v that spontaneously forms in the air.

The thermodynamic calculation of this entropy change is a standard one in introductory physics. The thermodynamic process from v to 0 corresponds to an adiabatic free expansion of a gas, which is assumed to be an ideal gas. The macrostate of the gas changes from an initial state where it occupies a volume $V - v$ to a final macrostate where it occupies a volume V , i.e., the gas freely expands into the hole. Since the internal energy of this isolated gas remains constant, the process is isothermal. To compute the entropy change, we imagine a reversible isothermal expansion of an ideal gas in which the volume changes from $V - v$ to V . For such a process, the conservation of energy dictates that the heat absorbed by the gas is equal to the work done by the gas: $dQ = pdV$. Combining this with the well-known ideal gas law, $pV = nRT$, the change in entropy in Eq. (19) becomes

$$S(0) - S(v) = nR \ln \left(\frac{V}{V-v} \right) \quad (20)$$

Finally, Eqs. (18) and (20) yield the hole-formation probability. Hence the probability $P(v)$ that a vacuous hole of volume v spontaneously forms in a room of volume V containing n moles of air is determined by

$$\frac{P(v)}{P(0)} = \left(1 - \frac{v}{V} \right)^{nR/k} \quad (21)$$

It is apparent that the formation of holes of macroscopic size is a highly improbable fantasy in our world where $k = 1.38 \times 10^{-23}$ J/K and $nR \gg k$. However, in a world where $k = 1.38 \times 10^{-2}$ J/K, finding large empty pockets in the air is a highly probable reality.

It is instructive to approximate the exact probability in Eq. (21) by expanding the slowly varying logarithm in Eq. (20) for the case where the holes are much smaller than the room ($v \ll V$): $\ln[1 - (v/V)] \approx -v/V$. Using this approximation and

$pV = nRT$, the entropy change in Eq. (20) becomes $\Delta S = pv/T$. The probability then assumes the eloquent form of a Boltzmann factor:

$$\frac{P(v)}{P(0)} = e^{-pv/kT} \quad (22)$$

Note that the volume of the room (V) and the amount of air (n), which are extensive variables, do not appear in this expression. Instead, the intensive variables (p and T) appear. Also note that the exponent, $nR/k = pV/kT$ in Eq. (21), is equal to the total number of air molecules in the room. The exponent, pv/kT in Eq. (22), is equal to the number of air molecules that left the hole. The hole probability is significant only if the hole size is an atomic volume, such as $v \approx (100\text{\AA})^3$, or if the air is extremely rarefied, such as $p \approx 10^{-20}$ atm.

Consider the large- k world. If $k = 1.38 \times 10^{-2}$ J/K, then in a room with an average standard pressure (1 atm) and temperature (300 K), the hole probability is $P(v) = \exp(-0.024v) P(0)$, where v is in cm^3 . In particular, the probability to find a hole of volume 50 cm^3 is $P(50 \text{ cm}^3) = 0.30 P(0)$. Thus, the equilibrium state of the air in this large- k world is far from static and consists of holes of varying sizes that regularly appear and disappear. The density of the air is quite time-dependent and nonuniform. Sometimes, all the air will be in one corner of the room, or on the floor, or on the ceiling. Such "vacuum fluctuations" occurring in the region of air around your mouth would leave you breathless!

Big Boltzmann and Small Avogadro

The large- k world seems strange because it is a small- N world. In this world, ordinary chunks of matter contain small number (N) of particles. To see this, recall the general relationship between Boltzmann's constant (k), Avogadro's number (N_A), and the gas constant (R): $kN_A = R$. Given the universal value $R = 8.31$ J/Kmole, then in a world where $k = 1.38 \times 10^{-2}$ J/K, Avogadro's number is $N_A = 6.02 \times 10^2$ mole $^{-1}$. Hence, one mole of matter contains 602 molecules. This explains the anomalous behavior exhibited by matter in this large- k world. The statistical fluctuations in a system containing 602 particles are large enough to be macroscopically observable. This sensitive dependence on the number (N) of particles can be seen more explicitly in Eqs. (12) and (21) by replacing nR/k with N . Note that in this big- k , small- N_A world, the measured values of macroscopic observables (such as molar masses, pressures, temperatures) would be similar to those measured in our world only if the mass of an atom were also a macroscopic quantity.

In our world, where $k = 1.38 \times 10^{-23}$ J/K and $N_A = 6.02 \times 10^{23}$ atoms/mole, nature provides us with macroscopic systems that seem complex because of the sheer enormity of the number of constituent particles. It is ironic and fortuitous that it is precisely this complexity of nature itself that is responsible for its underlying simplicity. The large- N statistics give rise to a determinism that guarantees that unnatural and sometimes dangerous fluctuations "never" seem to hap-

pen on the time scale of human observation. The comforting regularity and predictability of a world where equilibrium thermodynamics makes sense, and where the most probable state is the "only" state, makes for a safe and simple world. We the inhabitants of this world tend to take this for granted. Thank you, Boltzmann, that your constant is so small. Thank you, Avogadro, that your number is so large.

Conclusion

There are two fundamental ideas of physical statistics:

1. Probability of Macrostate: $P \propto \Omega$.
2. Entropy of Macrostate: $S = k \ln \Omega$.

These ideas are the building blocks of statistical physics. They can be folded smoothly into introductory physics, in complete harmony with thermodynamics, and with minimal effort. There is no need to introduce atomic models, quantum mechanics, mathematical statistics, Boltzmann factors, partition functions, or other intricacies of statistical mechanics.

Augmenting the standard thermodynamics presentation with the basic ideas of physical statistics can add insight and excitement to introductory physics. Blending statistics with thermodynamics provides a more holistic picture of the macroscopic world. Statistical physics illuminates the meaning of entropy and emphasizes the vital role played by the laws of chance in understanding the natural world. The statistical ideas open up a whole new thermodynamic territory that can be explored. The applications are interesting, and illustrate the power and the versatility of the statistical approach.

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7. H. Benson, *University Physics* (Wiley, New York, 1996), pp. 405-408.
8. R.A. Serway, *Physics for Scientists and Engineers* (Saunders, New York, 1996), p. 599.
9. The big- k world that we imagine is defined as a world that obeys the same laws of physics as the real small- k world. Furthermore, the values of macroscopic observables in the big- k world are identical to those measured in the small- k world. Macroscopic observables include temperature, pressure, heat, and entropy. Microscopic quantities include the mass of an atom, the velocity of an atom, and the number of atoms. Given this definition, the big- k world and the small- k world exhibit the same thermodynamics (macroscopic values), but have radically different statistics (fluctuations) and mechanics (microscopic values).
10. If $T = 300$ K in the big- k world, then $kT = 4.14$ J, which is the same order of magnitude as mgh for macroscopic masses and heights. This provides a microscopic explanation of levitation whereby the average kinetic energy (on the order of kT) of one air molecule or earth molecule is so large that, upon colliding with a body, the molecule can "kick" the body off the ground.