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The Boltzmann reservoir: A model constant-temperature environment

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The Boltzmann reservoir (BR) is a model constant-temperature environment that exhibits highly atypical thermodynamic behavior. Its microcanonical ensemble entropy is a linear, nonconcave function of its internal energy U, and its zero-work heat capacity is infinite. Its canonical partition function diverges because all possible energies are equally likely, so the microcanonical and canonical ensembles are *not* equivalent. If two BRs with the same temperature T_B are put in thermal contact, either can have any fraction of the total energy; i.e., there is no unique equilibrium state. If two BRs with different temperatures are in thermal contact, the higher temperature BR gives all its energy to the other. A BR's temperature cannot be changed by a heat process but, in principle, can be altered by a work process. These and other properties that challenge conventional wisdom provide thought-provoking examples for thermal physics courses. (© 2000 American Association of Physics Teachers.)

I. INTRODUCTION

Useful ways to model thermal reservoirs have been described recently by Prentis, Andrus, and Stasevich.¹ Their motivation was to present new and improved ways to obtain the Boltzmann factor of statistical physics. One of the interesting environments they proposed is the so-called Boltzmann reservoir (BR), a *hypothetical* model reservoir that assures a constant temperature in a non-BR system with which it is in thermal contact. The BR is described solely in terms of its energy spectrum,

$$U(n) = n\varepsilon$$
, with $\varepsilon > 0$ and $n = 0, 1, ..., (1)$

with degeneracy

$$\Omega(U) = b^n = b^{U/\varepsilon}, \quad \text{where } b > 1.$$
(2)

The parameter ε is the separation energy between adjacent degenerate energy levels, and *b* is a dimensionless constant. The BR's quantum state is denoted by the integer quantum number *n*. In Ref. 1, and also below, it is shown that for a chosen value of ε , the BR temperature is determined by the chosen value of *b*, and is independent of *n*, and thus *U*. This shows that the BR is indeed a constant-temperature system.

There are at least two reasons to examine the BR further.² First, although one expects a constant-temperature reservoir to be massive relative to the systems with which it interacts, and to store a relatively large internal energy, these features are not evident in the BR's defining Eqs. (1) and (2). Indeed, these equations contain no reference to the number of atoms in the BR, and a BR model can store *any* amount of energy, large or small. Finite energy storage precludes infinite size. This counter-intuitive property is but one of a number of intriguing BR properties that challenge conventional wisdom based on the behavior of *normal* macroscopic systems. Another is that the micro-and canonical ensembles give *different* results for the BR. It is hoped that by illustrating the unconventional, teachers and students can gain deeper insight into the conventional.

Second, macroscopically defined constant-temperature reservoirs are routinely assumed tools in thermal physics. Because they are assumed to store an infinite amount of energy, one cannot even write an expression for internal energy, say, as a function of temperature, and their properties are unknown. In contrast, the BR is a *microscopically* specified model that can store a *finite* internal energy and can be explored in depth using statistical mechanics. As the only known constant-temperature microscopic model that does not require the infinite size limit, it is an interesting addition to the list of tractable models in statistical physics.³

In what follows we address a *potpourri* of ideas relevant to BRs, including nonconcavity of entropy, infinite zerowork heat capacity, a non-invertible Legendre transformation, a canonical ensemble of reservoirs, inequivalence of the canonical and microcanonical ensembles, temperature change of a BR via a work process, and interactions between two BRs and between a BR and a *normal* reservoir. In Sec. II, we state and discuss nine properties (most of which are multifaceted) of BRs and in Sec. III we summarize what was learned. The reader who is more interested in the main ideas and results than the details can go directly to Sec. III.

II. PROPERTIES OF THE BOLTZMANN RESERVOIR

Property 1. Entropy, temperature, and heat capacity: The entropy S of a BR is a *linear* function of the *discrete* quantum number n, independent of the energy level spacing ε . The temperature T_B is constant and this implies infinite zerowork heat capacity C_{ε} .

Details: Linearity in n follows from the Boltzmann form of the entropy,

$$S(U) = k \ln \Omega(U) = \left(\frac{k \ln b}{\varepsilon}\right) U = (k \ln b)n, \qquad (3)$$

where *k* is Boltzmann's constant. For a given value of *n*, the smallest possible increase in $U, \Delta U = \varepsilon$, occurs for $\Delta n = 1$. The corresponding change in *S* is $\Delta S = (k \ln b)$. Because S(U) is linear in *U*, the finite difference ratio $\Delta S/\Delta U = (k \ln b)/\varepsilon$ is identical to the *formal* derivative $(\partial S/\partial U)_{\varepsilon}$, holding the parameter ε fixed. The constraint of fixed ε corresponds to energy transfer by a pure heat process—namely a process with zero-work on (or by) the BR. Thermodynamically this means that

$$T_B^{-1} = (\partial S / \partial U)_{\varepsilon}, \tag{4}$$

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and thus

$$T_B = \frac{\varepsilon}{k \ln b}.$$
(5)

Equation (5) shows how the parameter *b* determines the BR temperature T_B for a specified value of ε . Linearity and temperature constancy were discussed in Ref. 1.

From Eq. (5) it is clear that T_B is independent of U, and it follows that a BR has infinite heat capacity for a zero-work, pure heat process. That is, an energy exchange δQ between the BR and another system leaves the BR's temperature unaltered ($\Delta T_B = 0$), which implies that $C_{\varepsilon} = \delta Q / \Delta T_B$ is infinite. The label ε connotes a zero-work process. This completes the discussion of Property 1.

Property 2. The continuous variable approximation and the energy spectrum: For $0 < (b-1) \le 1$ and $\varepsilon \le kT_B$, S/kand $U/(kT_B)$ can be treated as continuous variables. Every region of the BR's energy spectrum is similar in the sense that the fractional increase in the number of states per unit energy interval is the same for all possible *n* and *U*. We assume the continuous approximation is valid throughout this article.

Details: For given fixed values of *b* and ε , the smallest increases in *S* and *U* occur for $\Delta n = 1$, whence $\Delta S = k \ln b$ and $\Delta U = \varepsilon = kT_B \ln b$, where the last step follows from Eq. (5). Therefore,

$$\Delta(S/k) = \Delta(U/(kT_B)) = \ln b = \xi \ll 1, \tag{6}$$

when

$$\xi \equiv b - 1 \ll 1. \tag{7}$$

Notice that $0 < \xi \le 1$, which means that *b* approaches unity from above. Equations (6) and (7) show that the changes in *S*/*k* and *U*/(*kT*_B) can be made arbitrarily small by choosing ξ sufficiently small. In this way the dimensionless entropy,⁴ (*S*/*k*), and the dimensionless ratio *U*/(*kT*_B) can be approximated as continuous variables. We work with dimensionless quantities to make our results independent of units.

Operationally, because Eqs. (1), (3), and (5) imply $U = T_B S$, we may write $dU = T_B dS$, with the understanding that this is equivalent to $d(U/(kT_B)) = d(S/k) \approx \xi \ll 1$. It is worth noting that Eqs. (1), (5), and (7) imply

$$\xi = \frac{\varepsilon}{kT_B} \ll 1. \tag{8}$$

Equation (8) shows that for a fixed value of T_B , if we select a decreasing sequence of ξ values, there is a corresponding decreasing sequence of ε values. Indeed, for $\xi \rightarrow 0$, we must also have $\varepsilon \rightarrow 0$ in order to keep T_B fixed. Notice that by suitable choices of $\varepsilon \ll 1$ and $\xi \ll 1$, one can obtain any desired temperature $T_B = \varepsilon/(k\xi)$ to lowest order in ξ .

Different regions of the spectrum are similar in the sense that the fractional increase in Ω , per unit energy interval, is independent of U; i.e., $(\partial S/\partial U)_{\varepsilon} = k[\partial(\ln \Omega)/\partial U]_{\varepsilon} = k[(d\Omega/\Omega)/dU]_{\varepsilon} = (k \ln b)/\varepsilon = \text{const.}$ This completes the discussion of Property 2.

Property 3. Canonical ensemble: The canonical partition function Z for a BR with temperature T_B diverges because the probability of finding the system in a state with energy U is the same for all U. The implied infinite energy fluctuations are consistent with the property of infinite heat capacity, and

are responsible for the inequivalence between the canonical and microcanonical ensembles for BRs.

Details: Consider first a BR for which $n \leq M$ and then let M become arbitrarily large. The partition function is Z_M $=\sum_{n}b^{n}\exp\left[-n\varepsilon/(kT_{B})\right]$, where the sum here and in the expressions below goes from n=0 to n=M. Equation (5) implies $b \exp[-\varepsilon/(kT_B)]=1$. Therefore $Z_M = \sum_n (1)^n = M + 1$. The probability of finding a system with energy $U=n\varepsilon$ is $P(U) = Z^{-1}b^n \exp[-n\varepsilon/(kT_B)] = Z^{-1} = (M+1)^{-1}$ for all n $\leq M$; i.e., P(U) is the same for each allowed energy U $\leq M\varepsilon$. In the limit $M \rightarrow \infty$, $Z_M \rightarrow \infty$ and $P(U) \rightarrow 0$ for all possible $U=n\varepsilon$. In the canonical ensemble, one has the identity, $C_{\varepsilon} = (\Delta E)^2 / (kT_B^2)$, where $(\Delta E)^2$ is the variance in the canonical energy. For finite M, the average energy in the ensemble is $\overline{E} = \varepsilon (M+1)^{-1} \Sigma_n n = \frac{1}{2} M \varepsilon$ because the sum is $\frac{1}{2}M(M+1)$. The variance $(\Delta E)^2 = (M+1)^{-1}\Sigma_n(n\varepsilon)^2$ $-(\frac{1}{2}M\varepsilon)^2$, and the inequality $\sum_n n^2 > \int_0^M y^2 dy = M^3/3$ im- $(\Delta E)^2 > M^2 \varepsilon^2 [(M-3)/12(M+1)].$ plies For М $\rightarrow \infty, (\Delta E)^2$ diverges as M^2 , consistent with the fact that each of the infinite number of energies 0, ε , 2ε ,... is equally likely. The infinite variance $(\Delta E)^2$ implies infinite heat capacity C_{ε} for $M \rightarrow \infty$, in accord with Property 1.

In contrast, for *normal* (*not* BR) macroscopic systems with $Z = \Sigma_E \Omega(E) \exp[-E/(kT)]$, $\ln Z \approx \ln \Omega(\hat{E}) - \hat{E}/(kT)$, where $\hat{E} \approx \bar{E}$, the system's average energy. This holds when the energy fluctuations are small relative to \bar{E} itself. In such cases, because the Helmholtz function is $A = -kT \ln Z$, this implies that $k \ln \Omega$, the *microcanonical* entropy, equals $(\bar{E} - A)T^{-1}$, a *canonical* ensemble entity. The latter reflects (but does not *prove*) that for *normal* systems, the canonical and microcanonical ensembles are equivalent.

However, for the rather *abnormal* BR, the infinite fluctuations in a canonical ensemble of BRs leads to the conclusion that canonical and microcanonical ensembles are *not* equivalent. The unbounded energy fluctuations can also be linked to thermodynamic instability, which is implied by the nonconcavity of S(U) described in Property 5.

Property 4. Legendre transform: Because the entropy S(U) is linear in U, the Helmholtz free energy A=U $-T_BS=0$. An equivalent statement is that the Legendre transformation of S with respect to U is formally zero. The inverse Legendre transform, leading from A to S, does not exist.

Details: By definition, $A = U - T_B S$. Because Eqs. (1), (3), and (5) imply $U = T_B S$, A = 0. The Legendre transformation of S(U) is defined as $\Psi(P) \equiv S - U(\partial S/\partial U)_{\varepsilon} = -A/T_B$, where $P \equiv (\partial S/\partial U)_{\varepsilon}$. Using Eq. (3), we obtain $\Psi = A = 0$. It is obviously impossible to construct S(U) from A; i.e., the inverse Legendre transform does not exist.⁵ Given that $A = -T_B \Psi$ and A is directly related to the canonical partition function, it is not surprising that a canonical ensemble of BRs leads to the mathematical difficulties described in Property 3.

Property 5. Nonconcave entropy: The linearity of S with U in Eq. (3) is not consistent with the thermodynamic stability requirement that S(U) be concave. As a consequence, if two BRs with the same ε , b, and T_B , but distinct internal energies $U \pm \Delta U$, are in thermal contact, forming an isolated

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composite system, no unique equilibrium state emerges. More specifically, all internal energy pairs $(U-\Delta U, U + \Delta U)$ have the same entropy and all are possible. Thus the number of possible final states is infinite.

Details: Concavity of S implies⁶ that if two systems of identical size and type, having internal energies $U - \Delta U$ and $U + \Delta U$ and entropies $S(U - \Delta U)$ and $S(U + \Delta U)$, interact thermally, and form an isolated composite system, they exchange energy until each has internal energy U. Their final total entropy will be 2S(U), where

$$2S(U) \ge S(U - \Delta U) + S(U + \Delta U),$$

with equality if and only if $\Delta U = 0.$ (9)

The strict inequality holds for all $\Delta U \neq 0$.

However, if two BRs with the same *b* and ε are in contact, then $S(U-\Delta U)+S(U+\Delta U)=(\varepsilon^{-1}k \ln b)[(U-\Delta U)+(U+\Delta U)]=(\varepsilon^{-1}k \ln b)(2U)=2S(U)=$ const for all ΔU . That is, in Eq. (9) the inequality is *never* satisfied and the equality is satisfied for all possible ΔU . It follows that all possible pairs $(U-\Delta U, U+\Delta U)$ have the same entropy, and all are possible final states. The lack of a unique equilibrium state is yet another sign of the BR's thermodynamic instability, which we encountered in Property 3 in terms of the infinite energy fluctuations and heat capacity.

Property 6. Interacting Boltzmann reservoirs: If two BRs have the same b, but different ε parameters, then they will have different temperatures. When two such BRs are put into thermal contact, forming an isolated system, energy will flow from higher to lower temperature until the higher temperature BR is empty of energy.

Details: Let BR₁ have $\varepsilon_1 > 0$ and $T_{B1} = \varepsilon_1 / (k \ln b)$ and BR₂ have $\varepsilon_2 > 0$ and $T_{B2} = \varepsilon_2 / (k \ln b)$, where $\varepsilon_1 < \varepsilon_2$. It follows from the foregoing that $S = k \ln b [U_1/\varepsilon_1 + U_2/\varepsilon_2]$, and the system entropy S is maximum when $U_1 \rightarrow U$ and $U_2 \rightarrow 0$.

Property 7. Interacting Boltzmann and normal reservoirs: Suppose a BR with temperature T_B is in thermal contact with a normal reservoir (defined below) having initial temperature T, and this composite system is isolated from the rest of the universe. If $T < T_B$ initially, the BR will transfer energy to the normal reservoir until either (a) T increases to the equilibrium temperature $T_e = T_B$ or (b) T increases to $T_e < T_B$ and the BR is empty of energy. If the BR has enough energy that $T_e = T_B$, then the BR can be described using the canonical ensemble at temperature T_B , but not at the normal reservoir's initial temperature T. If $T > T_B$ initially, the reservoir will transfer energy to the BR until $T_e = T_B$. When T_e $= T_B$, the conditions for a canonical ensemble of BRs exist, as in Property 3.

Details: A normal reservoir is defined here to be a system with internal energy U_R , entropy $S_R(U_R)$, and heat capacity C_R , with the property that its temperature $T = (\partial U_R / \partial S_R)_{\varepsilon}$ changes slowly with changes in U_R ; i.e., $\Delta T/T \approx \Delta U_R / (C_R T) \ll 1$ for $\Delta U_R \ll U_R$. In the composite system, with total energy U, denote the normal reservoir's energy by (U-E) and the BR's energy by E, where $E \ll U$ initially (i.e., the normal reservoir is relatively large). The total entropy of the composite system is $S_{\text{tot}} = S_R(U-E) + E/T_B$, and the equilibrium condition is $(\partial S_{\text{tot}} / \partial E)_{\varepsilon} = -1/T + 1/T_B = 0$. Also $(\partial^2 S_{\text{tot}} / \partial E^2)_{\varepsilon} = -1/(T^2 C_R) < 0$. The latter inequality assures that the total entropy's extremum is a maximum at equilibrium. Because T_B is fixed, the normal reservoir's temperature must vary in order to achieve the equilibrium condition $T_e = T_B$.

For $T < T_B$ initially, there is an energy transfer from the BR to the normal reservoir. If there is sufficient energy in the BR, equilibrium at $T = T_B$ can be reached. Otherwise, the BR will empty itself of energy, increasing S_{tot} as much as possible, and $T_e < T_B$. For $T > T_B$ initially, the energy transfer will be from the normal reservoir until its temperature equals T_B . If $T = T_B$ initially, the entropy S_{tot} is already maximized, so zero net energy transfer occurs and $T_e = T_B$. If $T_e = T_B$, we can consider a collection of BRs, each with an identical normal reservoir at temperature T_B —i.e., a canonical ensemble of BRs, as in Property 3.

In the case where $T_e < T_B$, one might naively consider a canonical ensemble of BRs with parameters b and ε , in contact with a reservoir R with constant temperature T $< \varepsilon/(k \ln b) = T_B$. In this case, $b \exp[-\varepsilon/(kT)] < 1$, whereupon the Z series converges formally to $Z = \{1 - b\}$ $\times \exp[-\varepsilon/(kT)]^{-1}$ and the average energy is U(T) $= \varepsilon \{ b^{-1} \exp [\varepsilon/(kT)] - 1 \}^{-1}$. This argument suggests that the BR behaves as a normal thermodynamic system. However, the discussion above shows that $T_e < T_B$ only if the BR transfers all its energy to the normal reservoir, so the canonical ensemble becomes a collection of BRs, each with U=0. Furthermore, the normal reservoir's temperature has changed from T to T_e , where T_e depends explicitly on how much energy the BRs had initially. These characteristics deviate substantially from the normal conditions and tenets of the canonical ensemble.

Property 8. Work and heat processes: If the energy level spacing ε is a function of an externally controllable variable (e.g., volume or magnetic field), the temperature T_B of a BR can be modified in principle by an adiabatic work process that alters ε . In contrast, heat processes change U by altering n for fixed ε . For an infinitesimal reversible work process $\delta W = S dT_B$, and for a combination work plus heat process, the heat capacity of a BR can be positive, negative, or zero.

Details: From Eqs. (3) and (5), we saw that $U = T_B S$. Thus $dU = T_B dS + S dT_B$. For a reversible heat process, $\delta Q = T_B dS$, and from the first law of thermodynamics, $dU = \delta Q + \delta W$. These equations imply $\delta W = S dT_B$. Equations (3) and (5) also lead to $T_B dS = \varepsilon \Delta n$ and $S dT_B = n d\varepsilon$. Thus a heat process changes the thermodynamic state of the system by changing its quantum state n, without altering the BR's energy spectrum. In contrast, an adiabatic reversible work process modifies the level separation ε without changing the quantum state n.

Along an arbitrary reversible path called π , we can write $\delta Q = T_B (\partial S/\partial T_B)_{\pi} dT_B \equiv C_{\pi} dT_B$ and $\delta W = S dT_B$, where C_{π} is the BR's heat capacity along the path π . Eliminating dT_B from the latter two equations, we obtain $\delta Q = (C_{\pi}/S) \delta W$. Assuming n > 0, then S > 0, and if δQ and δW have the same algebraic sign, then $C_{\pi} > 0$; if δQ and δW have opposite signs, then $C_{\pi} < 0$; and if $\delta Q = 0$ with $\delta W \neq 0$, then $C_{\pi} = 0$. The latter result is familiar; it holds for any reversible adiabatic work process in any system.

Property 9. Boltzmann factor: For any BR, $\Omega(U) = \exp(U/kT_B)$, and for an ensemble of nonreservoir systems in thermal contact with this BR, the probability of the system being in state *s* with energy E_s is $P(E_s) = Z^{-1}$

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 $\times \exp[-E_s/(kT_B)]$. This is the Boltzmann factor and Z is the canonical partition function.

Details: Equations (3) and (5) imply that $\Omega(U)$ $= \exp(U/kT_B)$. A consequence of the postulate of equal a priori probabilities is that the probability that a system in thermal contact with such a BR occupies state s with energy E_s is proportional to $\Omega(U-E_s)$, which can be put in the form $\exp[U/(kT_B)]\exp[-E_s/(kT)]$.^{1,7} Writing $P(E_s)$ $= Z^{-1} \exp\left[-E_s/(kT)\right],$ the normalization condition $\Sigma_s P(E_s) = 1$ shows that $Z = \Sigma_s \exp[-E_s/(kT_B)]$; i.e., the normalization factor Z is the canonical partition function. This finding is in agreement with that in Ref. 1 for a two-level system in contact with a BR, and with the observation therein that the result generalizes to other systems in thermal contact with a BR.

III. CONCLUSIONS

In order to maintain a constant temperature, a BR's entropy must be linear in the internal energy U and its zerowork heat capacity must be infinite. Although one normally envisions a reservoir as a large mass of material and arbitrarily large internal energy, there is no restriction on the size of the internal energy U of a hypothetical BR. Rather, its spectrum is such that the quantity $[(d\Omega/\Omega)/dU]_{\varepsilon}$ $= 1/(kT_B)$ is the same for all parts of the spectrum. This is very different from the typical case, where temperature increases and the latter ratio decreases with increasing energy. Further light is shed on the BR by considering an ensemble of BRs at their *natural* temperature $T_B = \varepsilon/(k \ln b)$. This is a collection of such BRs in thermal contact with any reservoir at temperature T_B . The structure of the BR's energy spectrum is such that the probability of finding it with energy Uis independent of U. This is consistent with the finding that $T = T_B$ independent of the region of the BR's spectrum that is involved.

In the canonical ensemble, $A = -kT_B \ln Z$, and Z diverges for a BR at temperature T_B , which implies $A \rightarrow -\infty$, in conflict with the thermodynamic result $A = U - T_B S = 0$. The lesson to be learned here is that the canonical ensemble formalism fails for a BR. In addition, because the microcanonical ensemble, typified by Eqs. (3) and (5), yields a well-defined entropy, this is an example where the two ensembles are not equivalent. The reason is that energy fluctuations in the canonical ensemble are infinite. This, in turn, can be traced to the fact that linearity in U means that S(U) is not concave, and this implies that a BR is not thermodynamically stable. Because A is the Legendre transform of S(U), the result A = 0 means that this Legendre transform is not invertible namely, one cannot construct S(U) from a knowledge of A.

If two reservoirs are linked to one another, one expects energy to flow from higher to lower temperature. For actual finite, *approximate* reservoirs, this would lead ultimately to thermodynamic equilibrium at an intermediate temperature. However, if a BR is put in contact with a normal reservoir namely a large system with high heat capacity—the energy exchange moves T toward T_B . If $T < T_B$ initially and there is not sufficient energy in the BR, the BR will simply give up all its internal energy to the normal reservoir. The BR's temperature remains T_B until the last joule of energy is transferred. If the BR has enough energy initially, then the normal reservoir achieves temperature $T_e = T_B$. For two BRs, no such compromise is possible because each reservoir maintains its initial temperature even as it gains or loses energy.The higher temperature BR will give all its energy to the lower temperature one.

Although heat processes cannot change the temperature of a BR, in principle a work process can do so by changing ε , the spacing between adjacent energy levels. That is, the temperature of a "heat reservoir" can be changed by an adiabatic work process. This variation in ε can occur without altering the BR's quantum state *n*. In contrast, heat processes change *n* with ε unaltered. For combined heat and work processes, the concomitant heat capacity can be positive, negative, or zero.

The BR enables one to quickly obtain the Boltzmann factor and the canonical ensemble from the microcanonical formalism. As observed in Ref. 1, the latter avoids the need for assumptions about constant temperature, the use of series expansions, and the so-called reservoir limit. These are notable points, which underscore the BR's potential value as a tool in statistical physics.

Prentis, Andrus, and Stasevich¹ have made an important contribution to thermal physics by modeling various reservoir environments. The Boltzmann reservoir is (to this author) the most interesting of their proposed environments because of its thought-provoking properties. By its very nature, a model reservoir that maintains strictly constant temperature amid finite energy exchanges exhibits thermodynamic behavior that is not conventional. The Boltzmann reservoir model illustrates this point well. It suggests that the common assumption of constant-temperature reservoirs, though helpful in thermal physics analyses, implies very weird properties for the reservoirs.

Because the BR is not based on a Hamiltonian, there is no reason to believe that it models *any* real system. Nevertheless, as the only known strictly constant-temperature microscopic model, it adds an intriguing example to the list of tractable statistical mechanical models. To the extent that its aberrant properties can bring a deeper appreciation of normal thermodynamic behavior, the Boltzmann reservoir offers the possibility of being a helpful teaching and learning tool in thermal physics courses.

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