Four Paradoxes Involving the Second Law of Thermodynamics

D. P. Sheehan
University of San Diego, dsheehan@sandiego.edu

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Four Paradoxes Involving the Second Law of Thermodynamics[1]

D. P. SHEEHAN

Department of Physics, University of San Diego, San Diego, CA 92110

Abstract — Recently four independent paradoxes have been proposed which appear to challenge the second law of thermodynamics [1-8]. These paradoxes are briefly reviewed. It is shown that each paradox results from a synergism of two broken symmetries — one geometric, one thermodynamic.

Keywords: physics — thermodynamics

1. Introduction

The second law of thermodynamics is empirical. It has no fully satisfactory theoretical proof. This being the case, its absolute validity depends upon its continued experimental verification in all thermodynamic regimes. Physical processes involving broken symmetries have been standard touchstones by which its validity has been tested [9-11]. Recently, four simple paradoxes have been posed which appear to challenge it [1-8]. In each, the universe consists of an infinite isothermal heat bath in which is immersed a blackbody cavity. Within each cavity, steady-state, non-equilibrium thermodynamic processes create spontaneous asymmetric momentum fluxes which are harnessed to do steady-state work. If one demands the first law of thermodynamics be satisfied by these systems, then apparent contradictions with the second law result. Laboratory experiments and numerical simulations have corroborated theoretical predictions and have failed to resolve the paradoxes in favor of the second law [1-8]. In this paper, it is shown that a broken symmetry in each of these four systems' thermodynamic properties allows asymmetric momentum fluxes to arise spontaneously, and that these can be harnessed to perform work utilizing a second broken symmetry in each system's geometry. By illuminating this characteristic shared by these paradoxes, it is hoped that their resolutions will be expedited.

It may be thought that asymmetries such as these are thermodynamically forbidden and that each system must relax to an equilibrium characterized by spatial homogeneity. This is not the case. In fact, "equilibrium" does not forbid spatial gradients so long as they are *steady-state* ones. For example, the

[1]Editor's note: This article has been accepted on the basis of an evaluation by a referee with expertise in thermodynamics who concludes that this article is well written and should be published to stimulate further investigation of these apparent paradoxes. However the referee also believes that further work will indicate that the problem does not lie with violation of the second law of thermodynamics.

asymmetric momentum fluxes to be introduced shortly in Systems II, III, and IV are no more than steady-state pressure gradients. Equilibrium (steady-state) pressure gradients are ubiquitous in nature. For instance, they are standard features of gravitationally-bound, isothermal, static atmospheres on idealized planets. In a uniform gravitational field, one can write the gas pressure as a function of vertical height, z, as $p(z) = p_o exp[-mg(z-z_o)/kT]$, where m is the mass of the gas molecule, kT is the thermal energy, g is the local gravitational acceleration, and p_o is a fiduciary pressure. Clearly, this atmosphere possesses a vertical pressure gradient at equilibrium. Similarly, the pressure gradients in Systems II-IV are steady-state structures, but unlike the atmospheric gradient which is *static* and due to a static potential gradient (gravity), these pressure gradients are *dynamically* maintained by the continuous effluxes from two surfaces having different activities toward the cavity gas. Furthermore, these pressure gradients can do work.

In the next section, the four paradoxes are reviewed briefly and in Section 3 they are discussed in the context of broken symmetries. Detailed descriptions of the paradoxes are found elsewhere [1-8].

2. Four Paradoxes

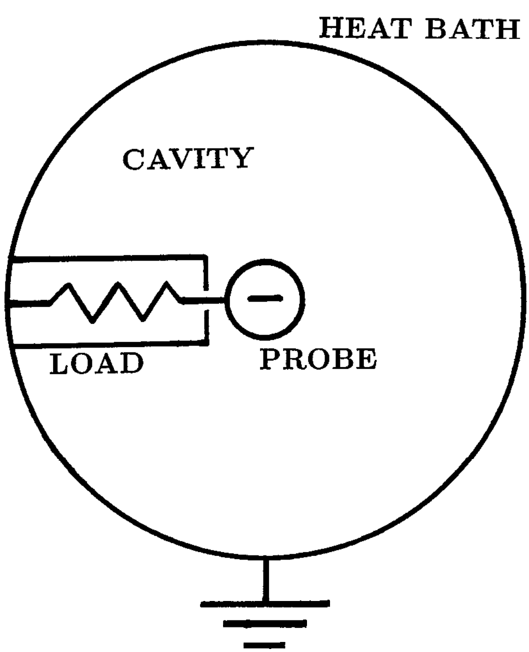

Fig. 1. Schematic of paradoxical system I. The probe bias is assumed negative.

2.1 System I

System I [1, 4-6] consists of a blackbody cavity containing a low-density plasma and an electrically conducting probe connected to the walls through a load, as shown in Figure 1. The load may be conservative (*e.g.* a motor) or dissipative (*e.g.* a resistor). The probe and load are small enough to represent minor perturbations to the cavity properties. The walls are grounded to the heat bath both thermally and electrically ($V_{ground}=0$). The potential between the bulk plasma and the cavity walls — the plasma potential, V_p — may be positive or negative depending on the work function and temperature of the walls, and the plasma type and concentration. For an electron-rich plasma and in the absence of any net current to the plasma or walls, V_p may be estimated by equating the Richardson emission, J_R from the walls to random electron flow from the plasma into the walls [12]:

$$J_R = AT^2 exp\left(-\frac{e\Phi}{kT}\right) exp\left(\frac{eV_p}{kT}\right) = \frac{nev_e}{4} \tag{1}$$

Here Φ is the wall's work function, T is temperature, V_p is the plasma potential, v_e is the average electron thermal speed, k is the Boltzmann constant, m_e is the electron mass, n is the plasma particle density, and A is the Richardson constant (about $6–12 \times 10^5$ (A/m^{2}K^2) for pure metals). Under either equilibrium or non-equilibrium conditions, V_p will be non-zero except for very specific plasma parameters; in particular, $V_p = 0$ at the critical density, $n_c = (4AT^2/ev_e)$ $exp\,[-e\Phi/kT]$, as derived from Eq. (1).

The probe will achieve a potential with respect to the plasma and walls depending on its temperature, resistance to ground (load resistance, R_L), and the current to it. Since it is nearly in thermal equilibrium with the walls, the probe is self-emissive and, therefore, electrically floats near the plasma potential so long as R_L is large [13]. If $V_p \neq 0$, a current can flow continuously from the probe, through the load, to ground. This current represents an asymmetric momentum flux. The generated power may be expressed as $dW/dt = I_L^2 R_L \approx (V_p^2/R_L)$. The entropy production rate is $dS/dt = (1/T)(dW/dt) \approx (V_p^2/R_L T)$; this will be positive (negative) for a purely dissipative (conservative) load. Laboratory experiments corroborate this effect [1, 4-5]. Note: this paradox is not limited to systems with thermionically emitting walls and probe; any plasma with a non-zero floating potential appears viable [6]. The paradox can be brought into sharper relief by placing a switch between the probe and the load. When the switch is open, the probe is physically disconnected from the walls (ground) and will electrically charge as a capacitor to the plasma floating potential. When the switch is closed, the probe will discharge as a capacitor through the load and plasma, achieving the non-vero voltage depicted in Fig. 2 of Ref. 1. With an ideal switch, this charging and discharging of the probe through the load can be repeated indefinitely.

If this system does steady-state work on the load while maintaining spatially steady-state temperature and species concentration profiles, and if the first law of thermodynamics is satisfied, then a paradox involving the second law naturally develops. Formally, the first law states: $[\Delta Q-\Delta W]_{hb} = -[\Delta Q-\Delta W]_c$, where hb refers to the heat bath and c refers to the cavity. The heat bath supplies heat, but does no work, so $\Delta W_{hb}=0$. If the load is conservative and each part of the cavity is at a steady state temperature, then $\Delta Q_c=0$. (It is assumed, without further justification, that there are no net phase changes or chemical reactions in the cavity.) Returning to the first law, since $\Delta W_{hb}=0$ and $\Delta Q_c=0$, this leaves $\Delta Q_{hb} = \Delta W_c$. The cavity does positive work, so $\Delta W_c = \Delta Q_{hb} < 0$; in other words, the work performed by the load is drawn as heat from the heat bath, a reasonable result.

Now consider the second law. Entropy is an additive thermodynamic quantity so the entropy change for the universe can be written: $\Delta S_{universe} = \Delta S_{hb} + \Delta S_c$. Since $\Delta Q_c = 0$, one has for the cavity, $\Delta S_c = \Delta Q_c / T = 0$. (Equivalently, one may argue that entropy is a state function and the closed cavity is in a steady state — having no net phase changes, chemical reactions, temperature or volume changes, the number of microstates available to it is fixed — thus the entropy of the cavity is time invariant, and so $\Delta S_c = 0$.) With $\Delta S_c = 0$, one is left with: $\Delta S_{universe} = \Delta S_{hb} = \Delta Q_{hb}/T_{hb} < 0$. This violates the second law of thermodynamics, namely that for any spontaneous thermodynamic process, $\Delta S_{universe} \geq 0$. If one replaces R_L with a dissipative load, the second law is violated still, since a forbidden, permanent temperature gradient has been established between the load and the cavity ($T_{load} > T_c$). Note that this system is not in thermal equilibrium; this process is irreversible. In order to use validly equilibrium thermodynamic relations, the work must be performed "slowly."

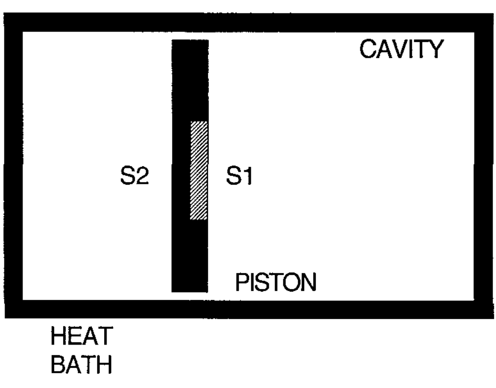

Fig. 2. Schematic for paradoxical systems II and III.

This can be achieved to any degree of precision desired by adjusting the load resistance. Similar arguments establish the remaining three paradoxes. Note also, neither this system nor the other three utilize standard thermodynamic cycles or a low temperature heat reservoir.

2.2 System II

Paradoxical system II[2] is a mechanical analog to system I. Too, it consists of a blackbody cavity surrounded by the heat bath. The cavity contains a low-density ionizable gas, *B*, and a frictionless, two-sided piston (See Figure 2). As before, Richardson emission greatly exceeds ion emission for all surfaces, giving an electron-rich plasma with a negative plasma potential. The majority of the piston is of identical composition as the walls (surface type 2, *S*2), however, on one piston face is a small patch having a different work function (surface type 1, *S*1). It is small in the sense that it is relatively unperturbing to global plasma properties. The work functions of *S*1 and *S*2 and the ionization potential of *B* are ordered as: $\Phi_1 \gtrsim I.P. > \Phi_2$. Plasma production is straightforward: electrons are "boiled" out of the metal (Richardson emission) and ions, created by surface ionization, are accelerated off the metal surface by the electron negative space charge. Ions, in turn, ease the electrons' space charge impediment, thus releasing a quasi-neutral plasma from the surface. Actually, if $V_p < 0$, this is essentially a charge-neutralized, low-energy ion beam leaving the surface. In fact, this plasma can be roughly considered to be an unmagnetized, three-dimensional *Q*-plasma with a sliding hot plate [14].

The ordering $\Phi_1 \gtrsim I.P. > \Phi_2$ allows, with appropriate plasma density and temperature, and surface areas $((SA)_2 \gg (SA)_1)$, the following: surface 1 ionizes *B* well and recombines it poorly while surface 2 ionizes *B* poorly, but recombines *B* well. Surface 2 dominates plasma properties by virtue of its greater surface area $((SA)_2 >> (SA)_1)$, therefore, the net flux of *B* to any surface is predominantly neutral *B*. Surface 1 will be relatively unperturbing to cavity plasma conditions if the *S*1 ion current into the plasma is much less than the total *S*2 ion current. The electron emission off *S*2 exceeds that off *S*1 by a factor $exp[(\Phi_2\text{-}\Phi_1)/kT]$. The electron current density from each surface is given by Eq. (1).

Because of the differences between neutral, electronic, and ionic masses and the different currents of each leaving *S*1 and *S*2, a steady-state asymmetric momentum flux density (a "net pressure difference," ΔP), is sustained between piston faces. It has been shown that this pressure difference is roughly [2]

$$\Delta P \approx -\frac{p_{i,2} n_n kT}{2} - \frac{\pi}{4}\frac{m_e v_e}{e} J_{R,1} + m_i \frac{n_n v_n}{4} p_{i,2}\sqrt{-\frac{2eV_p}{m_i}} \qquad (2)$$

where $p_{i,2}$ is the ionization probability of *B* on *S*2, n_n is the neutral density, $J_{R,1}$

is the Richardson current density from $S1$, m_i is the ion mass, and v_n is the neutral thermal velocity. The first, second, and third terms represent neutral, electronic, and ionic pressures, respectively. Laboratory experiments corroborate steady-state differential thermionic emission from different surfaces under blackbody conditions [2]. Numerical simulations, using realistic physical parameters, indicate the pressure effect is small, but significant [2]. If the piston moves slowly ($v_{piston} << v_n$) and performs work quasi-statically, it generates steady-state $(dW/dt)_{piston} = \Delta P(SA)_1\, v_{piston}$, and produces negative entropy at the rate, $dS/dt = (1/T)\ (dW/dt)_{piston}$. Notice that, even in the absence of a plasma potential, V_p, the paradoxical effect persists so long as the ionization probability of the two surfaces are distinct.

2.3 System III

Paradoxical system III[7,8] is the chemical-mechanical analog of system II. It consists of a blackbody cavity with piston into which is introduced a small quantity of dimeric gas, A_2. The cavity walls and piston are made from a single material, surface type 2 ($S2$), except for a small patch of a different material, surface type 1 (S1), on one piston face, as shown in Fig. 2. (Note $S1$ and $S2$ here are distinct from those in system II.) The chemical model for this system assumes the following: a) the gas phase density is low such that gas phase collisions are rare compared with gas-surface collisions, however, it is sufficiently high that rms pressure fluctuations are small compared with the average pressure; b) all species contacting a surface stick and later leave in thermal equilibrium with the surface; c) the only relevant surface processes are adsorption, desorption, dissociation, and recombination; d) the fractional surface coverage is low, so adsorption and desorption are first order processes; e) A_2 and A are highly mobile on all surfaces and may be treated as a two-dimensional gas; and f) atomic and molecular species are retained sufficiently long on any surface to achieve close to chemical thermal equilibrium in the surface phase. These conditions are physically realistic and have been shown to be self-consistent [8]. For these conditions, it can be shown that, in principle, $S1$ and $S2$ can simultaneously desorb different ratios of A and A_2 in a steady-state fashion. However, since two A's together impart $\sqrt{2}$ times the impulse to the piston as does a single A_2 (all leaving in thermal equilibrium with the surface), asymmetric momentum fluxes can be sustained between the piston surfaces. (Another way to view this is: equipartition of energy does not imply equipartition of linear momentum.) The pressure imbalance on the piston faces can be used to perform work in a similar manner to system II.

For low surface coverage where desorption is a first order process, the desorption rate ratio for A and A_2, $R_{des}(A_2)/R_{des}(A) \equiv \alpha$, is given by [15-17]:

$$\alpha \equiv \frac{R_{des}(A_2)}{R_{des}(A)} = \frac{n(A_2)}{n(A)}\,\frac{F(A)}{F(A_2)}\exp\{\frac{\Delta E_{des}(A) - \Delta E_{des}(A_2)}{kT}\} \qquad (3)$$

Here $\Delta E_{des}(A_j)$ is the desorption energy of A_j; $n(A_j)$ is the surface concentrate of A_j(m^{-2}) and $F(A_j) \equiv (f/f^*)_{A_j}$ is a ratio of partition functions. f is the partition function for the species in equilibrium with the surface, and f^* is the species-surface partition function in its activated states. For real surface reactions, $F(A_j)$ typically ranges between roughly 10^{-3}–10^4. Experimental values of desorption energy, ΔE_{des}, typically range from about 1 kJ/mol for weak physisorption up to about 400 kJ/mole for strong chemisorption.

The ratio α varies as $0 \leq \alpha \leq \infty$ depending on the values of the several variables in Eq. (3). Experimental signatures of differential α's (some under quasi-blackbody conditions) are abundant [18-21]. If $\alpha_1 \neq \alpha_2$, and if the instantaneous fluxes of A and A_2 from $S2$ each greatly exceed those from $S1$ so that $S1$ can be treated as an impurity (*i.e.* $R_{des}(2,A_2)/R_{des}(1,A_2) >> (SA)_1/(SA)_2$ and $R_{des}(2, A)/R_{des}(1, A) >> (SA)_1/(SA)_2$, then a steady-state difference in momentum flux density (net pressure difference, ΔP) can be sustained between piston faces. Here $(SA)_j$ is the surface area of the j *th* surface. This pressure difference can be expressed:

$$\Delta P = \left(2-\sqrt{2}\right) m_A v_A R_T(A) \left[\frac{\alpha_2 - \alpha_1}{(2\alpha_1+1)(2\alpha_2+1)}\right] \tag{4}$$

where $R_T(A)$ is the total flux density of A onto a surface, $R_T = [n(c,A)v_A + 2n(c,A_2)v_{A_2}]/\sqrt{6\pi}$. Here $n(c,A_j)$ is the cavity concentration of A or A_2. In the limit that $\alpha_2 >> 1 >> \alpha_1$, the greatest pressure difference is obtained; it is roughly: $\Delta P \approx 0.3 m_A v_A R_T (A)$. This pressure difference is steady-state since the dynamic chemical processes giving rise to it are steady-state. If this pressure difference is significantly greater than the statistical pressure fluctuations in the cavity, then, in principle, it can be exploited to do steady-state work. The power and entropy production rates here are the same as for system II. As for system II, the piston must move *slowly* compared with the thermal velocity of gaseous A_2. Note that, when the piston moves, the volume and surface phases for this system are not in equilibrium; in fact, they are in steady-state non-equilibrium.

This chemical system has been simulated numerically [8]. Closed-form, analytic rate equations have been developed and solved simultaneously using realistic physical parameters. Solutions confirm the possibility of this paradoxical effect; it is probably small — but significant — and appears viable over a wide range of physically accessible parameters. Laboratory systems displaying this effect are currently being sought.

2.4 System IV

To introduce System IV, consider an everyday scenario: from the same height, drop a glass marble onto two different surfaces, for instance, a hard wood floor and a soft rug. The marble inelastically rebounds to different heights, demonstrating the different inelastic (endoergic) responses of the two surfaces. Inherently, these collisions are non-equilibrium processes. Analogous non-equilibrium behavior is observed on the atomic scale: it is well known that hyperthermal gas-surface collisions can excite energy states associated with internal degrees of freedom of either the collider or target — *e.g.* rotational, vibrational and electronic modes, phonons, plasmons — thereby rendering the collisions inelastic [22-26]. In fact, a number of standard surface diagnostics are based upon just such characteristic inelastic reponses. In contrast, at thermal equilibrium gas-surface collisions must, on average, be *elastic,* otherwise more direct contradictions with the second law arise. ("Hyperthermal" collisions are those with impact energies far above thermal energies — typically a few tenths of an eV up to about 100 eV in energy.) Studies indicate energy transfer efficiencies from hyperthermal colliders to targets can range from a few percent to over ninety percent of incident atom kinetic energies [22]. Motivated by these observations, a simple, idealized system is considered: a strongly gravitating rod, whose ends have different inelastic responses to hyperthermal impacts by a particular gas, is placed at rest in a blackbody cavity with that gas. When steady state is reached, gas continuously falls hyperthermally onto the rod, inelastically rebounds to different degrees from the rod ends, and is rethermalized in the blackbody cavity. The particle fluxes to and from both rod ends are identical, but the momentum fluxes are different, giving rise to a net force on the rod. If released, the rod accelerates in the direction of the net force and, in principle, can be harnessed to do mechanical work.

The idealized system consists of: (i) an infinite heat bath; (ii) a large, spherical blackbody cavity; (iii) a low density gas in the cavity; and (iv) a rod gravitator. The rod (length $2L_g$) has symmetric mass density $\rho(x) = \rho(-x)$ about its center at $x = 0$, but its end surfaces ($S1$ and $S2$) are composed of two materials distinct in their inelastic responses to gas atoms (mass m_A). In other words, for $S1$ and $S2$ one can write the inelastic response functions as distinct: $v_f(1,v_i) \neq v_f(2,v_i)$. The inelastic response function for surface j, $v_f(j,v_i)$, maps the velocity of a particle before impact, v_i, onto its velocity after impact, v_f.

The rod represents a minor perturbation to the overall cavity properties. Its gravitational scattering length L_s is much smaller than the cavity scale length, L_c. As a result, N_s, the ratio of the average number of wall collisions a gas atom undergoes (N_{wall}) to the average number of rod collisions (N_{rod}) it undergoes, is large; that is, $N_s \equiv N_{wall}/N_{rod} \approx (L_c/L_S)^2 >> 1$. Gas colliding with the cavity walls, regardless of its history, is diffusely scattered (for rough walls), well mixed, and fully thermalized within a few wall collisions. For the rod at rest at the cavity center then, gas populations infalling from the walls to $S1$ and $S2$ may be taken to be fully thermal and identical in temperature and density. In terms of the velocity distribution functions, this is: ($f_I(1,|v|) = f_I(2,|v|)$ and $f_{II}(1,|v|) = f_{II}(2,|v|)$. The velocity distributions for gas infalling from

$x = \pm L_c$ are half-Maxwellians, $f_I(j,v)$. When they arrive at $S1$ and $S2$ they are velocity space compressed due to their falls through the gravitational potential, becoming $f_{II}(j,v)$. The rebounding distributions, $f_{III}(j,v)$, are distinct for the two surfaces. After climbing out of the gravitational well, the velocity space expanded distributions $f_{IV}(j,v)$ are rethermalized at the walls. Gravitationally bound gas, $f_V(j,v)$, forms an atmosphere around the rod. The cavity contains blackbody radiation and gas whose mean free path is comparable to or greater than the distance between the rod and the walls. Gas kinetic energy fluxes are much smaller than radiative energy fluxes; in other words, blackbody radiation dominates the system's energy transfers. Small surface temperature variations arising from inelastic collisions are quickly smoothed out by compensating radiative in- or effluxes. This model is valid over a wide range of physically realistic parameters and is well approximated by a planet-sized gravitator in a low density gas housed in blackbody cavity of solar system dimensions. In the following analysis, the rod will be treated one dimensionally; however, it can be shown, in retrospect, that the following results generalize to two and three dimensions.

The net force on the stationary rod can be determined from conservation of linear momentum, accounting for both incident and reflected particle fluxes. As discussed previously, since $f_I(1,|v|) = f_I(2,|v|)$ and $f_{II}(1,|v|) = f_{II}(2,|v|)$, by symmetry, the net force on the rod (at rest) due to incident gas is zero. However, the net force due to the inelastically reflecting gas need not be zero since $f_{III}(1,|v|) \neq f_{III}(2,|v|)$ and $f_{IV}(1,|v|) \neq f_{IV}(2,|v|)$. Consider the $S1$ rod end. The incident particle flux density which infalls from the walls at $x = -L_c$ to $S1$ at $x = -L_g$ is $N_i(1) = \int_0^\infty v f_{II}(1,v)dv$. From conservation of mass, the incident particle flux density is equal to the reflected particle flux density: $N_i(1) = N_f(1) = \int_0^{-\infty} v f_{III}(1,v)dv$. The differential momentum flux density for the rebounding gas (taken at $x = -L_g$) is $dF_p(1) = [m_A v]dN_f(1) = m_A v^2 f_{III}(1,v)dv$. Only atoms with $v \leq -v_{esc}$ will climb completely out of the gravitational potential well; the remainder will fall back to the rod, form an atmosphere, and eventually evaporate as the ($v \leq -v_{esc}$)-tail of $f_v(1,v)$. Accounting for the gravitational back-reaction of the gas on the rod as it climbs out of the gravitational well, the total average steady-state momentum flux density on surface $S1$ is:

$$F_P(1) \approx M_A \int_{-v_{esc}}^{-\infty} v\sqrt{v^2 - v_{esc}^2}\,[f_{III}(1,v) + f_V(1,v)]dv \tag{5}$$

The approximation ($\approx$) is due to the finite cavity size; in the limit of $-L_c \longrightarrow -\infty$, the expression becomes exact. For $S2$, $-v_{esc} \longrightarrow +v_{esc}$ and $-\infty \longrightarrow +\infty$ in the limits of integration. In the limit of a tenuous atmosphere, the momentum flux density due to the ($|v| \geq |v_{esc}|$)-tail of $f_V(j,v)$ is negligible; in fact, $f_V(j,v)$ is negligible for systems with low gas densities, n_A, and with inelastic response functions, $v_f(j,v_i)$ which do not shift $|v_f|$ significantly below $|v_{esc}|$.

By conservation of linear momentum, the average net momentum flux density (pressure) on the rod as a whole is $\Delta F = F_p(1) - F_p(2)$. If $v_f(1,v_i) \neq v_f(2,v_i)$ in the velocity range of the colliding gas, then except under extremely contrived conditions, one has $\Delta F \neq 0$. In other words, under steady-state thermodynamic conditions, a stationary, gravitating rod with different inelastic responses on its ends can, in principle, experience a non-zero, steady-state force when placed in a suitable gas. If the rod is released, this force can be harnessed to do work at the expense of the heat bath, as discussed previously.

3. Two Broken Symmetries

Each paradox arises due to a synergism between two broken symmetries — one thermodynamic and one geometric. Each is necessary, but alone insufficient. A broken geometric symmetry is constructed into each system. System I possesses almost perfect radial symmetry; this symmetry is broken by the electrical connection from the probe, through the load, to ground. In the case of disconnection, the probe will randomly and radially receive current from the walls through the plasma and radially and randomly return this current to the walls back through the plasma. This is the equilibrium (fully symmetric) case. If the load is connected, however, the probe's return current has an alternate path to ground and the radial symmetry of the current flow is broken. Analogously, in systems II-IV, the piston's constrained, one-dimensional motion effectively reduces (breaks) the systems' three dimensionality to one.

These broken geometric symmetries are necessary to exploit each system's broken thermodynamic symmetry. The latter may be identified by observing which thermodynamic property, if symmetrized, destroys the paradoxical effect. In system I, the effect is lost if the plasma potential is *symmetrized* to $V_p = 0$. (It is assumed here that for self-emissive probes the floating potential for a probe is equal to the plasma potential [1,13].) This can be made zero in several ways including : i) ceasing plasma production; ii) achieving the critical plasma density, n_c; or iii) creating a mass-symmetric plasma — a negative ion plasma [27]. More generally, the non-zero V_p can be considered due to either a) the fundamental mass asymmetry between electron and ions; or b) that surfaces preferentially emit electrons or ions depending on values of their surface temperature and work function, and gas ionization potential.

In system II, the paradoxical effect is lost if the work functions of $S1$ and $S2$ are equal: $\Phi_1 = \Phi_2$. Then, the electronic, ionic and neutral momentum flux densities from all surfaces are identical, rendering zero the pressure differential between piston faces. In general, the symmetry condition, $\Phi_1 = \Phi_2$, is difficult to achieve unless $S1$ and $S2$ are the same material — a trivial case.

In system III, the effect is lost if the desorption rate ratios for $S1$ and $S2$ are equal: $\alpha_1 = \alpha_2$. As seen from Eq (3), this requires either fine tuning in values of surface density, partition functions, and desorption energies, or that $S1$ and $S2$ be identical substances. As with Φ in system II, the symmetry condition, $\alpha_1 = \alpha_2$, is difficult to achieve unless $S1$ and $S2$ are identical. In system IV, the effect is lost if $v_f(1,v_i) = v_f(2,v_i)$. This is most easily accomplished by symmetrizing the rod's composition.

Each broken thermodynamic symmetry (in V_p, Φ, α, or $v_f(j,v_i)$) occurs naturally under either equilibrium or non-equilibrium conditions and allows momentum flux asymmetries to arise. Via the broken geometry symmetry, the broken thermodynamic symmetry is exploited to do work. Both broken symmetries appear to be necessary since the thermodynamic quantities V_p, Φ, α, and $v_f(j,v_i)$ are spatially homogeneous (independent of spatial variables); therefore, by themselves they are insufficient to direct momentum fluxes to do work. This requires the broken spatial (geometric) symmetry; in System I it is accomplished by an electrical conductor and in Systems II-IV by a piston. From these four examples[1], a conjecture is induced: Given a spatially homogeneous thermodynamic property that causes a macroscopic asymmetric momentum flux (under equilibrium or non-equilibrium conditions), a second broken geometric symmetry is necessary and, if suitably arranged, can be sufficient to do work solely at the expense of a heat bath in violation of the second law.

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[1] It is noted that system IV was not used in inducing this conjecture; on the contrary, it was deduced from it. As a challenge, the author cooked it up to test whether the conjecture induced from systems I-III could hold for gravitational systems as it seemed to apply for electromagnetic ones. Apparently, it can.

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