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Reply to ''Comment on 'Dynamically maintained steady-state pressure gradients' ''

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A reply is made to Duncan's Comment [T. L. Duncan, Phys. Rev. E **61**, 4661 (2000)] on my earlier paper [D. P. Sheehan, Phys. Rev. E **57**, 6660 (1998)] in which he raises an apparent second-law paradox arising from dynamically maintained, steady-state pressure gradients. Resolutions to this paradox are considered in light of current theoretical and experimental understanding.

Duncan raises an interesting and germane paradox involving the recently described dynamically maintained, steady-state pressure gradient (DSPG) [1] and the second law of thermodynamics. There appear to be only three logically possible resolutions to Duncan's paradox; they are (I) The DSPG is physically impossible to achieve, hence the paradox does not arise; or (II) The DSPG is physically possible, but some currently unidentified physical effect preserves the second law; or (III) The DSPG is physically possible and the second law of thermodynamics can be violated.

Understandably, (III) is the least palatable and least likely scientifically. Possibly no physical law other than the first law of thermodynamics has more support than the second. Since an exhaustive list of the physical contingencies surrounding this paradox probably cannot be verified by theory alone and since scientific truths are ultimately empirical in nature, (III) should remain unacceptable unless overwhelming experimental evidence is found or a working version of a second law violator is constructed. Likewise, however, the second law is itself inherently empirical, therefore (III) cannot logically be ruled out either, unless either (I) or (II) is shown to be correct.

In considering (I) and (II), both of which preserve the second law, one should consider three issues: (i) Duncan's paradox appears to be only one of a larger class of second-law paradoxes which rely on different physical processes than his [2–5]; (ii) ''standard'' resolutions to second-law paradoxes appear to fail for this one; and (iii) there appears to be some experimental support for the possibility of a DSPG, which is the crux of the paradox.

First, Duncan's paradox is not an isolated puzzle. There are at least three other analogous paradoxes involving the second law, all based on different physical processes [2–5]. Each arises from the asymmetric transfer of momentum between surfaces, mediated by a working gas. In each, a paradox arises because of two broken symmetries, one thermodynamic and one geometric. In Duncan's paradox the thermodynamic symmetry is broken in the desorption flux rate ratio, α, and the geometric symmetry is broken by paving the turbine blades with different surface types, S_1 and S_2. In the other paradoxes the broken thermodynamic symmetries are in the mass ratios of negative (electron) to positive (ion) plasma species (plasma paradox 1 [2,4]), surface work functions (plasma paradox 2 [3]), and the surface trapping probability of a gas undergoing surface collisions (gravitational paradox [5]). The broken geometric symmetries are similar to that in Duncan's paradox.

Second, Duncan's paradox has been considered carefully by a large number of chemists and physicists; thus far, it remains unresolved. In the Appendix are compiled all resolutions currently advanced for it, as well as responses to them.

Third, there appears to be experimental support for the possibility of a DSPG. Since the second law has not been well investigated experimentally in the extreme thermodynamic regimes under which these paradoxes arise, it seems likely that further investigation into the DSPG effect may lead to new insights into the second law and perhaps shed light on the entire class of paradoxes to which it belongs. In its simplest incarnation, the DSPG arises due to the differential dissociation of diatomic molecules into monomers at submonolayer concentrations on different surfaces and to their differential thermal desorption rate ratios [1]. These give rise to a steady-state, spatially anisotropic pressure gradient which apparently can, according to Duncan, be exploited to perform steady-state work solely at the expense of a heat bath and in violation of the second law. Steady-state pressure gradients are not thermodynamically forbidden and are, in fact, common—for example, we exist in one right now: the earth's atmospheric pressure gradient. What makes the DSPG so odious is that it can have a preferred spatial direction and, therefore, can be harnessed to perform steady-state work; this is in contrast to, for instance, atmospheric pressure gradients which are radially symmetric and, therefore, incapable of doing steady-state work.

There is no explicit experimental evidence for the DSPG, however, neither does it appear that it has ever been explicitly sought. The physical conditions under which it should be most viable are extreme: low gas density, submonolayer surface coverage, blackbody conditions, two or more surfaces which are differentially chemically reactive toward the same cavity gas, and possibly high temperatures ($T \gtrsim 1500\,\mathrm{K}$). Candidate chemical systems have been proposed elsewhere [1].

Although explicit evidence for the DSPG is lacking, there is experimental evidence for its underlying process, specifically, for differential dissociative adsorption and desorption of light molecules from different surfaces. Consider, for example, the results of Otsuka, Ihara, and Komiyama [6] involving dissociation and desorption of H_2 from Ta and W.

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They found in the low gas density limit where gas phase equilibrium could not be assumed—the same constraint as for the DSPG—that, under identical temperatures and pressures, H_2 dissociative adsorption and desorption were more probable and rapid on W than on Ta and, therefore, in bulk more endothermic on W than on Ta. They emphasized that at these low pressures, gas phase equilibrium could not be assumed and that the production of H radicals was set by surface reaction rates, rather than by gas phase equilibrium. These results strongly corroborate the mechanism of the DSPG and Duncan's paradoxical effect for two reasons. First, if this differential endothermicity for hydrogen on W and Ta persists under mutual blackbody conditions, it suggests that one could establish a permanent temperature difference between W and Ta surfaces within the same blackbody cavity which, in principle, could be harnessed to perform steady-state work, this undercutting the second law. Second, this differential endothermicity amounts to a differential momentum flux density between W and Ta arising from the differential effluxes of H_2 and H. Again, were this to persist under blackbody cavity conditions, it would lead directly to Duncan's paradox. Other gas-surface chemical results also corroborate the DSPG [7–11].

Therefore, in light of (1) the existence of other unresolved analogous paradoxes; (2) the apparent failure of "standard" resolutions to resolve Duncan's paradox; and (3) the corroborative experimental data for the DSPG, it appears likely that the resolution of these paradoxes may uncover new and interesting insights into the second law.

APPENDIX: RESOLUTIONS

The following are all purported resolutions to Duncan's paradox known to this author. [Note: Resolutions (n) and (o) may appear less "robust" than others; these are included for the sake of completeness since they are the resolutions most commonly offered by chemists and physicists.]

(a) *Symmetry resolution*. Surface equilibrium constants [K_i in Eq. (14) in Ref. [1]], and the surface desorption ratios [α in Eq. (15) in Ref. [1]] must be the same for all surfaces.

Response. This resolution conflicts with both theory and experiment [1,7–13].

(b) *Equilibrium resolution*. The system will (or must) eventually relax to an equilibrium characterized by no net pressure gradients. In other words, the system will "find a way" to avoid the offending pressure gradients.

Response. This resolution lacks a physical mechanism and, therefore, is both nonexplanatory and unsatisfactory. Furthermore, since relaxation to equilibrium is mediated by the second law in the first place, by invoking the necessity for equilibrium as a resolution, one tacitly invokes the second law to uphold itself. This is circular reasoning and is logically unsound.

(c) *Catalyst resolution*. The two surfaces, S_1 and S_2, are catalysts and, therefore, they cannot influence the ultimate cavity gas phase concentrations which must be the unique and standard gas phase equilibrium. As such, the desorption fluxes off the surfaces must be identical; therefore, there can be no pressure gradients, hence no paradox.

Response. The precept that catalysts cannot affect equilibrium concentrations is misapplied here since this is a non-

equilibrium system. More to the point, the rate equations [Eq. (1)] are quite general; they describe *any* steady-state system, be it an equilibrium or nonequilibrium one. Their solution for this chemical system demonstrates that two distinct, steady-state, local, nonequilibrium gas phase concentrations can be maintained simultaneously in a single cavity.

(d) *Detailed balance resolution*. The principle of detailed balance guarantees identical adsorption and desorption fluxes from S_1 and S_2, therefore precludes the offending pressure gradients.

Response. Applied to gas-surface systems, the principle of detailed balance says that at equilibrium the adsorption rate of a given species onto a surface must equal its desorption rate from that surface. This principle is dubiously applied to the present system since the system is not at equilibrium. For this system to be at equilibrium would require that $\alpha(1) = \alpha(2)$, however, it has been shown that $\alpha(1) \neq \alpha(2)$ [see Eq. (15) in Ref. [1]]. In fact, experimental evidence for detailed balance far from equilibrium is absent from the scientific literature and evidence for it even at equilibrium is scarce at best. As summed up by Masel [14]: "Only a small number of [gas-surface] systems have been definitely shown to obey detailed balancing...[and] they are really measurements that are being done at conditions close to equilibrium. Thus from the available data it is unclear whether detailed balance works at conditions far from equilibrium." And, as others have cautioned, Masel warns against indiscriminately applying detailed balance to nonequilibrium systems: "If the state of the adsorbate is in any way different during adsorption and desorption, the forces on the molecules will be different during adsorption and desorption. Therefore, detailed balancing will not hold. Unfortunately, when one does a nonequilibrium experiment, one often finds that something changes between when the molecules adsorb and when they desorb. Hence, it is often unclear whether one can apply detailed balancing in a nonequilibrium situation." This is the case here.

In this model, adsorbed species A and A_2 collide on the surfaces and achieve surface equilibrium due to their long surface residence times relative to their dissociation and recombination times; that is, for S_1 and S_2 one has $\tau_{\text{diss}}, \tau_{\text{recomb}} \ll \tau_{\text{res}}$. (This is embodied in model constraints e and f in Ref. [1].) Since A and A_2 can be entirely distinct chemical species with respect to their interactions with surfaces S_1 and S_2, there is no *a priori* reason to presume that either their surface equilibrium constants or their desorption rates should be identical for the different surfaces. In fact, for this model they are different. Furthermore, since the gas phase lacks collisionality, it is unable to determine its own species concentrations, but instead must rely on the surface desorbates. If S_1 and S_2 have distinct desorption ratios then, by definition, the gas phase is not at global equilibrium.

Furthermore, to assert that detailed balance applies to nonequilibrium systems is to risk being impaled on a different horn of the second law: failure of a system to move toward equilibrium. A gas-surface chemical system moves from nonequilibrium toward equilibrium precisely because it does not satisfy detailed balance. To impose detailed balance on nonequilibrium systems would essentially forbid them from achieving equilibrium; in essence, the imperative of detailed balance on nonequilibrium systems could itself con-

stitute a violation of the second law. On the other hand, to presuppose the system is in equilibrium in order that detailed balance *does* apply is logically invalid since it begs the question; that is, it is to assume that which one wishes to prove.

In summary, it is not clear that the principle of detailed balance can be meaningfully applied to this system since the principle itself lacks adequate experimental support in nonequilibrium systems and is theoretically suspect for such systems.

(e) *Prohibited pressure gradient resolution*. Pressure gradients cannot be maintained in steady state since they will relax via hydrodynamic forces.

Response. Hydrodynamic forces are absent in this chemical system since it is in the molecular flow regime. Furthermore, pressure gradients are, in fact, allowed even in the hydrodynamic regime. For instance, in a static, isothermal, gravitationally bound atmosphere (as on a planet) the pressure varies exponentially with altitude—this system clearly has a pressure gradient, even at equilibrium.

(f) *Fluctuation resolution*. The pressure gradients considered here are statistical fluctuations and are ineffectual for doing work.

Response. Numerical analysis using realistic physical parameters—such as are given in Appendix B in Ref. [1]—demonstrates the contrary: that the purported pressure gradients are far in excess of those which can arise due to statistical fluctuations and they are sufficient to do macroscopic work.

(g) *Freeze-out resolution*. The heat lost from the turbine blades to do mechanical work will eventually cool the blades to the point that the requisite surface reactions are shut down, foiling the paradoxical effect.

Response. In this model, the radiative power flux greatly exceeds the gas kinetic energy flux to any surface such that any variations in surface temperature due to differential desorption are quickly erased by radiation. For the system considered in Appendix B of Ref. [1], for instance, the maximum temperature variation at S_1 or S_2 is, at most, on the order of a few parts in 10^6. This small temperature variation is insufficient to cancel the paradoxical effect.

(h) *Asymmetric heating resolution*. Asymmetric heating of surfaces by asymmetric chemical reactions creates symmetrization of the pressure over S_1 and S_2, negating the paradoxical effect.

Response. As in the ''freeze-out'' resolution directly above, the temperature variation between S_1 and S_2 is at most a few parts in 10^6. Assuming roughly ideal gas behavior, this should reduce the pressure gradient by a commensurate amount: roughly a few parts in 10^6 of the average cavity pressure. Since the paradoxical pressure differential between S_1 and S_2 can be comparable in magnitude to the average gas pressure in the cavity—that is, on the order of a million times larger than the asymmetric heating pressure variation—it is untenable that this pressure variation would cancel the paradoxical one.

(i) *Transience resolution*. The system might start robustly, but it must eventually ''run down'' and achieve thermal equilibrium. The DSPG is only a transient.

Response. The DSPG is derived from the explicit starting assumption that steady state has been reached. This is incompatable with ''run down'' or transience. In particular, the rate equations [Eqs. (1)–(7) in Ref. [1]], from which the DSPG are derived, are quite general and apply to equilibrium and nonequilibrium systems alike, so long as they are in steady state. Their solution—the DSPG—is, therefore, an inherently steady-state phenomenon. Furthermore, as discussed above, other steady-state (nontransient) pressure gradients, such as atmospheric gradients are thermodynamically allowed. The DSPG is distinguished from these standard gradients in its offense to the second law solely by its spatial anisotropy. This feature is not addressed by this resolution.

(j) *Electrochemical resolution*. Surfaces 1 and 2 are coupled electrically, as are electrodes in a battery, such that they electrochemically communicate and mutually adjust desorption products so as to preclude any pressure gradients.

Response. This resolution lacks a mechanism and is, therefore, unsatisfactory. Furthermore, it is easily sidestepped. Surfaces 1 and 2 can be electrically insulated from each other—e.g., with the insulator alumina—without altering the primary results. (The low-density cavity gas is also a good electrical insulator for the exposed surfaces.)

(k) *Heat engine resolution*. This ''heat engine'' does not operate between two heat reservoirs at different temperatures; therefore, it is theoretically impossible.

Response. This resolution begs the question similarly to the ''equilibrium'' resolution above since the two-reservoir requirement is itself predicated on the validity of the second law. In fact, there should be a slight temperature gradient between the cavity and heat bath (see ''asymmetric heating'' resolution above) arising from the work done in the cavity. It is against this temperature gradient that heat flows continuously from the heat bath into the cavity.

(l) *Absence of evidence resolution*. Careful gas-surface studies have been conducted for nearly a century. These have surveyed systems over many orders of magnitude in temperature and pressure and have cataloged hundreds, if not thousands, of gas-surface combinations. That this paradox has not been discovered yet should raise strong skepticism as to its possibility.

Response. Indeed, this should engender skepticism, however, this does not constitute a resolution. The absence of evidence is not evidence of absence. The specific thermodynamic regime necessary for this system— a low pressure regime where surface coverages are low (less than a monolayer) and surface effects are important, where gas phase collisions are rare, but where statistical pressure fluctuations are small compared with the average pressure—is difficult to achieve, even by design. Indeed, numerous gas-surface studies have been performed (and some of these have yielded tantalizing results from the point of view of this paradox [6–11]), however, most studies have been carried out (i) at relatively high pressures where standard gas phase equilibrium existed or where submonolayer surface coverages could not be assumed; or (ii) in a geometry which did not approximate a sealed blackbody cavity; or (iii) where only a single chemically active surface was involved. Furthermore, given the many critical physical parameters which must be matched between the surface types and the gas, given the relatively narrow density regime over which the process may be viable (see Tables Ia, b, and Fig. 1 in Ref. [1]), and given the minuteness of the physical effect to be observed, it is not

surprising that this phenomenon has not been discovered accidentally.

(m) *Spin resolution*. The turbine blades are angularly accelerated by gas-surface collisions. This process should continue until the blades spin at relativistic speeds. This is implausible, therefore, the paradox must be flawed.

Resolution. It is easy to show from kinetic analysis that the unloaded turbine blades will accelerate to a terminal angular velocity at which the average tangential velocity of the blades is about 25% of the thermal speed of the gas. If the turbine is loaded down (e.g., with an electrical generator), the terminal velocity will be reduced. This terminal velocity is reached as the leading side of the blade ''catch up to'' and ''bats'' gas molecules ahead of the blade up to suprathermal speeds, thereby losing blade momentum, while the trailing side of the blade ''outruns'' the molecules in the gas velocity distribution, thereby losing its propulsion. As blade speed increases, these two effects eventually reduce the net propulsive force on the blade to zero; acceleration ceases and terminal velocity is reached.

(n) *Nonexistence resolution*. The DSPG cannot occur; therefore, there is no paradox.

Response. Lacking clarification with particulars, this resolution is nonexplanatory and is logically void since it merely states a desired outcome without justification. Furthermore, it does nothing to refute the positive derivation of the DSPG [1].

(o) *Second law violation resolution*. The DSPG cannot occur because it violates the second law; therefore, there is no paradox.

Response. See response to ''nonexistence'' resolution directly above.

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