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# Dynamically maintained steady-state pressure gradients

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In a sealed blackbody cavity with gas, pressure gradients commonly take three forms: (a) statistical fluctuations, (b) transients associated with the system relaxing toward equilibrium, and (c) equilibrium pressure gradients associated with potential gradients (such as with gravity). In this paper, it is shown that in the low-density (collisionless) regime, a fourth type of pressure gradient may arise, this due to steady-state differential thermal desorption of surface species from chemically active surfaces. This gas phase is inherently nonequilibrium in character. Numerical simulations using realistic physical parameters support the possibility of this gas phase and indicate that these novel pressure gradients might be observable in the laboratory; candidate chemical systems are suggested. [S1063-651X(98)07406-6]

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## I. INTRODUCTION

Standard gas phase equilibrium assumes temporal and spatial homogeneity in thermodynamic quantities such as particle density, pressure, and temperature—aside, of course, from statistical fluctuations and those imposed by potential gradients (e.g., gravity) [1,2]. If the gas is collisional, homogeneity can be argued forcefully both theoretically—using quantum, statistical, and fluid mechanics—and also experimentally by appealing to countless laboratory studies. When gas phase collisions are rare compared with gas-surface collisions, however, standard gas phase equilibrium should not be taken for granted and serious account must be taken of chemical reactions of the gas with the confining walls. Particularly when the gas species has chemical reactivity with the surface, the nature of the gas phase is not obvious.

In this paper it is shown that in 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, a nonequilibrium gas phase may arise in which macroscopic pressure gradients can persist. Numerical simulations using realistic physical parameters support this hypothesis and indicate this gas phase might be observable in the laboratory.

Steady-state (equilibrium) pressure gradients are common in nature. For instance, they are standard features of gravitationally bound, isothermal, static atmospheres, such as those on idealized planets. In a uniform gravitational field, one can write the gas pressure as a function of vertical height, $z$, as $p(z) = p_0 \exp[-mg(z-z_0)/kT]$, where $m$ is the mass of the gas molecule, $kT$ is the thermal energy, $g$ is the local gravitational acceleration, and $p_0$ is a fiduciary pressure. Clearly, this atmosphere possesses a vertical pressure gradient. The pressure gradients discussed in this paper are also steady-state structures, but unlike the atmospheric gradient, which is an equilibrium structure due to a static potential gradient (gravity), the pressure gradient here is an inherently nonequilibrium structure that is dynamically maintained by the continuous gaseous effluxes from chemically dissimilar surfaces. Hereafter, ''dynamically-maintained steady-state pressure gradient'' will be abbreviated DSPG.

The DSPG represents a new type of pressure gradient. Also, it acts as a limiting thermodynamic case: one at extremely low gas pressures and surface coverages. This particular physical regime has not been explored carefully either theoretically or experimentally. Numerous gas-surface interaction studies have been performed, but most of these have been carried out (i) at relatively high pressures where standard gas phase equilibrium can be assumed or where submonolayer surface coverages cannot be assumed; or (ii) in a geometry that does not approximate a blackbody; or (iii) where only a single chemically active surface is involved.

This paper is organized as follows: in Sec. II rate relations are introduced for a general chemical system; approximate relations are then derived for the more specific DSPG model. In Sec. III, the pressure gradient is demonstrated and suggestions are made for laboratory systems that might exhibit it. Appendix A provides theoretical support for the simplified relations in Sec. II, and Appendix B describes a hypothetical system incorporating realistic physical parameters that display this effect. A number of variables will be used in this paper. The initial $i$ will refer to surface type, $j$ to chemical species; the subscripts ads, des, diss, and recomb will refer to the processes of adsorption, desorption, dissociation, and recombination of atomic or molecular species [e.g., $R_{ads}(i,A_j) = R_{ads}(1,A_2)$ is the adsorption rate of the $A_2$ molecules from surface type 1].

## II. CHEMICAL MODEL FOR DSPG

### A. General rate relations

Consider a sealed blackbody cavity into which is introduced a small quantity of dimeric gas, $A_2$. The cavity walls are made from a single chemically active material, surface type 2 ($S2$), except for a small patch of a different material, surface type 1 ($S1$). By definition, in steady state the average numbers of $A$ and $A_2$ on any surface and in the cavity volume are time invariant, i.e.,

$$\frac{dN(i,A_j)}{dt} = 0, \tag{1}$$

where the subscripts $i = 1, 2$, or $c$ stand for surfaces 1 or 2 or

the cavity volume; and $N$ is the average number of either species $A$ or $A_2$. Equation (1) can be expanded in terms of the various sources and sinks of $A$ and $A_2$:

$$\frac{dN(c,A)}{dt}=0=[R_{\text{des}}(1,A)-R_{\text{ads}}(1,A)](SA)_1+[R_{\text{des}}(2,A)$$

$$-R_{\text{ads}}(2,A)](SA)_2+[2R_{\text{diss}}(c,A_2)$$

$$-R_{\text{recomb}}(c,A)]V_{\text{cav}}, \quad (2)$$

$$\frac{dN(c,A_2)}{dt}=0$$

$$=[R_{\text{des}}(1,A_2)-R_{\text{ads}}(1,A_2)](SA)_1$$

$$+[R_{\text{des}}(2,A_2)-R_{\text{ads}}(2,A_2)](SA)_2$$

$$+\left[\frac{1}{2}R_{\text{recomb}}(c,A)-R_{\text{diss}}(c,A_2)\right]V_{\text{cav}}, \quad (3)$$

$$\frac{dN(1,A)}{dt}=0=[R_{\text{ads}}(1,A)-R_{\text{des}}(1,A)+2R_{\text{diss}}(1,A_2)$$

$$-R_{\text{recomb}}(1,A)](SA)_1, \quad (4)$$

$$\frac{dN(1,A_2)}{dt}=0=\left[R_{\text{ads}}(1,A_2)-R_{\text{des}}(1,A_2)+\frac{1}{2}R_{\text{recomb}}(1,A)\right.$$

$$\left.-R_{\text{diss}}(1,A_2)\right](SA)_1, \quad (5)$$

$$\frac{dN(2,A)}{dt}=0=[R_{\text{ads}}(2,A)-R_{\text{des}}(2,A)+2R_{\text{diss}}(2,A_2)$$

$$-R_{\text{recomb}}(2,A)](SA)_2, \quad (6)$$

$$\frac{dN(2,A_2)}{dt}=0=\left[R_{\text{ads}}(2,A_2)-R_{\text{des}}(2,A_2)+\frac{1}{2}R_{\text{recomb}}(2,A)\right.$$

$$\left.-R_{\text{diss}}(2,A_2)\right](SA)_2. \quad (7)$$

Here $R$ refers to adsorption, desorption, dissociation, or recombination rates [m$^{-2}$ s$^{-1}$ for surfaces and m$^{-3}$ s$^{-1}$ for volume]; and $(SA)_1$, $(SA)_2$, and $V_{\text{cav}}$ are the surface areas of $S1$ and $S2$, and the cavity volume, respectively [3].

Relations (2)–(7) are generally applicable and, in principle, can be simultaneously solved if given adequate thermodynamic information. For a cavity system with a short mean free path, there will be three distinct thermodynamic equilibria: two surface phases and the standard gas phase equilibrium. As the mean free path becomes comparable or long compared with cavity dimensions, however, standard gas phase equilibrium cannot be taken for granted. In fact, as will be shown, it can be absent.

### B. Chemical model

The following chemical constraints (a)–(f) will be assumed for the cavity system discussed above. These con-

straints are commonly assumed in gas-surface studies and are easily shown to be both valid and self-consistent within a broad parameter space.

(a) The gas phase density is low such that gas phase collisions are rare compared with gas-surface collisions. [In other words, the mean free path of gas atoms is very long compared with cavity scale lengths; i.e., $\lambda \gg L_{\text{cav}}$.] However, the average pressure is much greater than the rms pressure fluctuations; i.e., $P_{\text{cav}} \gg \delta P_{\text{rms}}$.

(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) 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.

(f) All species spend much more time in the surface phases than in the gas phase. In other words, the characteristic time any species spends on a surface before desorbing (its desorption time, $\tau_{\text{des}}$) is much longer than its thermal-velocity transit time across the cavity, $\tau_{\text{trans}}$. Also, for $S1$ the time scales for dissociation of $A_2$ and recombination of $A$ is short compared with the desorption time. (These allow the surface concentrations of $A$ and $A_2$ to be in approximate chemical equilibrium.)

### C. Simplified system relations

For this chemical model, the six general rate relations [Eqs. (2)–(7)] can be solved simultaneously or they can be recast into five equations in the six variables, $n(i,A_j)$, with one variable taken as independent. [Reasoning leading from model constraints (a)–(f) to Eqs. (8)–(12) is found in Appendix A.] Equations (2)–(7) are recast into

$$n(c,A)\simeq\frac{\sqrt{6\pi}}{v_A\tau_{\text{des}}(2,A)}n(2,A), \quad (8)$$

$$n(c,A_2)\simeq\frac{\sqrt{6\pi}}{v_{A_2}\tau_{\text{des}}(2,A_2)}n(2,A_2), \quad (9)$$

$$K(1)\simeq\frac{n(1,A_2)}{n^2(1,A)}, \quad (10)$$

$$K(2)\simeq\frac{n(2,A_2)}{n^2(2,A)}, \quad (11)$$

$$\frac{v_A}{\sqrt{6\pi}}n(c,A)+\frac{2v_{A_2}}{\sqrt{6\pi}}n(c,A_2)$$

$$\simeq\frac{1}{\tau_{\text{des}}(1,A)}n(1,A)+\frac{2}{\tau_{\text{des}}(1,A_2)}n(1,A_2). \quad (12)$$

Here $\tau_{\text{des}}$ is given by

$$\tau_{\text{des}}(i,A_j)\simeq\frac{1}{\nu_0}F(i,A_j)\exp\left[\frac{\Delta E_{\text{des}}(i,A_j)}{kT}\right] \quad (13)$$

TABLE I. Thermodynamic and operating parameters for representative DSPG system.

| | |
|---|---|
| Molecular weight $A_2$ | 40 amu |
| Atomic weight $A$ ($m_A$) | 20 amu |
| Atomic radius $A$ ($r_A$) | $5 \times 10^{-10}$ m |
| rms velocity $A_2$($v_{A_2}$) | 790 m/sec |
| rms velocity $A$ ($v_A$) | $1.1 \times 10^3$ m/sec |
| Cavity $A_2$ density [$n(c,A_2)$] | $2 \times 10^{16}$ m$^{-3}$ |
| Cavity temperature ($T$) | 1000 K |
| Cavity radius ($R$) | 0.1 m |
| $S1$ patch scale length | $10^{-3}$ m |
| Surface area ratio, $(SA)_2/(SA)_1$ | $10^9$ |
| $E(A-A)$ | 240 kJ/mole |
| Surface lattice frequency, $\nu_0$ | $10^{13}$ Hz |
| $A_2$ vibrational frequency, $\nu_{\text{vib}}$ | $10^{13}$ Hz |
| Monolayer density | $10^{19}$ m$^{-2}$ |

TABLE II. Thermodynamic surface parameters for representative DSPG system. All $\Delta E$'s are in kJ/mole.

| | Surface 1 | Surface 2 |
|---|---|---|
| $\Delta E_{\text{des}}(A)$ | 250 | 200 |
| $\Delta E_{\text{des}}(A_2)$ | 260 | 190 |
| $\Delta E_{\text{diss,act}}$ | 0 | 30 |
| $F(A)$ | $10^{-2}$ | $10^3$ |
| $F(A_2)$ | $10^3$ | 1 |
| $\gamma_{\text{diss}}$ | $10^{-1}$ | $10^{-9}$ |
| $\gamma_{\text{recomb}}$ | $10^{-6}$ | $10^{-1}$ |

and $K(i)$, the ratio of the surface densities of $A_2$ and $A$ under surface dissociative-recombinative equilibrium is given by [4,5]

$$K(i) \equiv \frac{n(i,A_2)}{n^2(i,A)} \simeq \frac{r_A v_A}{\nu_{\text{vib}}} \frac{\gamma_{\text{recomb}}(i)}{\gamma_{\text{diss}}(i)} \exp\left[\frac{\Delta E_{\text{diss,act}}(i)}{kT}\right]. \quad (14)$$

In theory, the surface equilibrium constant, $K(i)$, can vary as $0 \leq K(i) \leq \infty$; experimentally $K$ is well known to vary for different molecules, surfaces, and temperatures [6–9].

In Eqs. (8)–(14), $n(i,A_j)$ is the surface or volume number density of $A_j$; $v_{A_j}$ is the thermal speed of $A_j$ ($v_{A_j}$ is taken to be the same for gas and surface phases); $\nu_0$ is the characteristic vibrational frequency of the surface (typically $\nu_0 \sim 10^{13}$ Hz); and $F(i,A_j) \equiv (f/f^*)$ 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, $f/f^*$ typically ranges between roughly $10^{-3}$ and $10^4$. Here $\Delta E_{\text{des}}$ is the desorption energy (experimental values typically range from about 1 kJ/mol for weak physisorption up to about 400 kJ/mole for strong chemisorption); $T$ is temperature, $k$ is Boltzmann's constant, $\nu_{\text{vib}}$ is the attempt frequency for dissociation (roughly the $A_2$ molecular vibrational frequency and also typically equal roughly to the surface vibrational frequency; that is, $\nu_{\text{vib}} \sim \nu_0 \sim 10^{13}$ Hz). Here $\Delta E_{\text{diss,act}}$ is the energy of activation for dissociation of $A_2$ on the surface (typical values range from 0 kJ/mole to about 500 kJ/mole); $\gamma_{\text{diss}}$ is the probability of a molecular vibration leading to dissociation on the surface ($0 \leq \gamma_{\text{diss}} \leq 1$); $r_A$ is the atomic radius of $A$; and $\gamma_{\text{recomb}}$ is the probability of recombination for $A$-$A$ surface collisions ($0 \leq \gamma_{\text{recomb}} \leq 1$).

The meaning of Eqs. (8)–(12) can be inferred from inspection: Eqs. (8) and (9) are statements of conservation of $A$ and $A_2$ within the cavity; Eqs. (10) and (11) are statements of chemical equilibrium on $S1$ and $S2$; and Eq. (12) states conservation of total $A$ atoms on $S1$. With these five equations and with particular system parameters (e.g., those in Tables I and II), one can calculate the steady-state surface and volume species densities for this system. Note that Eqs. (10) and (11)

describe chemical equilibrium at $S1$ and $S2$, but that gas phase equilibrium is not guaranteed within this model.

### D. System limits

In addition to recasting the rate relations, the model constraints (a)–(f) in Sec. II B also place the following four limits on surface and volume densities:

*Limit 1:* The lower limit of cavity density is that at which statistical pressure fluctuations, $\delta P_{\text{rms}}$, remain negligible compared with the pressure difference, $\Delta P$. A standard relation between rms pressure fluctuations and the number of particles in a system, $N$, is given by [10,11] $\delta P_{\text{rms}}/P \sim 1/N^{1/3} \sim [1/n(c)L^3]^{1/3}$, where $L$ is the scale size of the system and $P$ is the average gas pressure. A criterion for rms pressure fluctuations to be negligible is $\delta P_{\text{rms}} \sim P/n(c)^{1/3}L_{S1} \ll \Delta P$, where $L_{S1}$ is the scale size of the small $S1$ patch.

*Limit 2:* The upper limit cavity density is that density at which the mean free path $\lambda$ still remains long compared with the cavity scale lengths. Roughly, it is: $\lambda \sim 1/\pi r_A^2 n(c) \gg L_{\text{cav}}$.

*Limit 3:* The upper limit surface species density, $n(i,A_j)$, is that at which the fractional surface coverage $\theta$ still remains much less than unity ($\theta \ll 1$).

*Limit 4:* The lower limit surface density $n(1,A)$ is set at that density for which the recombination time of $A$ on $S1$, $\tau_{\text{recomb}}(1)$, remains much less than the desorption times, $\tau_{\text{des}}(1,A_j)$.

### III. PRESSURE GRADIENT

The critical requirement for the DSPG is this: that in steady state, $S1$ and $S2$ desorb distinctly in the same environment simultaneously. This will occur if $\alpha(1) \neq \alpha(2)$. For low surface coverage where desorption is a first order process, the desorption rate ratio, $R_{\text{des}}(i,A_2)/R_{\text{des}}(i,A) \equiv \alpha(i)$, is given by [4,5]

$$\alpha(i) \equiv \frac{R_{\text{des}}(i,A_2)}{R_{\text{des}}(i,A)}$$

$$= \frac{n(i,A_2)}{n(i,A)} \frac{F(i,A)}{F(i,A_2)} \exp\left\{\frac{\Delta E_{\text{des}}(i,A) - \Delta E_{\text{des}}(i,A_2)}{kT}\right\}. \quad (15)$$

The ratio $\alpha$ varies as $0 \leq \alpha \leq \infty$. Experimental signatures of differential $\alpha$'s are abundant [12–18]. If $\alpha(1) \neq \alpha(2)$, the

cavity gas cannot be in standard gas phase equilibrium since this equilibrium must, by definition, be unique while the cavity gas phase is twained by two distinct $\alpha(i)$.

The DSPG effect can arise in any sealed blackbody cavity where $\alpha(1) \neq \alpha(2)$, regardless of the relative surface areas of $S1$ and $S2$. However, a simple case to analyze is one in which the surface area of $S1$ is much less than that of $S2$; that is, $(SA)_1 \ll (SA)_2$. In this case, if the total desorptive fluxes of $A_2$ and $A$ from $S2$ each far exceed the total fluxes from $S1$, then $S2$ will almost completely determine the surface and volume inventories of $A$ and $A_2$, regardless of the behavior of $S1$. (This could be argued cogently from LeChatlier's principle.) The conditions that the instantaneous fluxes of $A$ and $A_2$ from $S2$ each greatly exceed those from $S1$ can be written as

$$\frac{R_{\text{des}}(2,A_2)}{R_{\text{des}}(1,A_2)} \gg \frac{(SA)_1}{(SA)_2} \qquad (16)$$

and

$$\frac{R_{\text{des}}(2,A)}{R_{\text{des}}(1,A)} \gg \frac{(SA)_1}{(SA)_2}. \qquad (17)$$

Effectively, $S1$ is made an arbitrarily small ''impurity'' in the chemical dynamics of the cavity.

Under conditions (16) and (17), and assuming all species leave all surfaces thermally, the pressure difference between $S1$ and $S2$ ($\Delta P = P_1 - P_2$) can be expressed as

$$\Delta P = m_A v_A R_{\text{des}}(1,A) + m_{A_2} v_{A_2} R_{\text{des}}(1,A_2) - m_A v_A R_{\text{des}}(2,A)$$
$$- m_{A_2} v_{A_2} R_{\text{des}}(2,A_2) \qquad (18)$$

or it can be written in terms of the desorption ratios $\alpha$ as

$$\Delta P = (2-\sqrt{2}) m_A v_A R_T(A) \left[ \frac{\alpha(2)-\alpha(1)}{[2\alpha(1)+1][2\alpha(2)+1]} \right], \qquad (19)$$

where $R_T(A)$ is the total flux density of $A$ onto a surface, $R_T(A) = (1/\sqrt{6\pi})[n(c,A)v_A + 2n(c,A_2)v_{A_2}]$. Notice from Eq. (19) that so long as $\alpha(1) \neq \alpha(2)$, then $\Delta P \neq 0$. If $\Delta P$ persists over a distance scale $\Delta x$, the pressure gradient is roughly $\nabla P \sim \Delta P / \Delta x$.

One may draw an analogy between this gaseous nonequilibrium pressure gradient and one that can arise in a photon gas. Consider a blackbody radiator placed between two large parallel plates held at different temperatures ($T_1$ and $T_2$). The radiation pressure gradient across such a thermally nonconducting blackbody (scale length $\Delta x$) would be on the order of $\nabla P \sim (S_1 - S_2)/c\Delta x \sim \sigma(T_1^4 - T_2^4)/c\Delta x$, where $S$ is the Poynting flux, $\sigma$ is the Stefan-Boltzmann constant, and $c$ is the speed of light. (The introduction of a molecular gas would complicate this analysis via well-known photophoretic effects [19].) Both the DSPG and this photonic $\nabla P$ are steady-state nonequilibrium structures, however, whereas the photonic case requires an enforced temperature difference, the DSPG arises spontaneously under isothermal conditions.

## Candidate systems

Laboratory searches for the DSPG effect should be possible. The broadest base of technical knowledge for molecular-surface interactions exists for light diatomic molecules (e.g., $H_2$, $N_2$, $O_2$, CO) with transition metals (e.g., Fe, Ni, Pt, Cu, Pd, Au, Ag) [6]. Polyatomic molecules with preferred dissociation channels, organic or biological molecules which are cleaved or fused by specific enzymatic surfaces might also provide candidates. In principle, this effect can be sought at low temperatures. Surface desorption and dissociation energies can be less than 0.1 kJ/mole for van der Waals interactions [20]. One might expect this effect to be manifest at or below room temperature, perhaps even below 100 K for weakly bound van der Waals molecules such as $Ar_2$ or $He_2$, which exhibit very weak binding even to metal surfaces [20–24]. An experimental signature of this should be a variation in the second virial coefficient for a van der Waals gas depending on the composition or structure of the confining surface. Numerical analysis (Appendix B) suggests DSPG-viable temperatures ($T \leq 2000$ K) and pressures ($P \leq 10^{-6}$ torr) are within current experimental capabilities.

## APPENDIX A

In this appendix, support is given in the following points [(i)-(v)] for the reduction of the general equilibrium relations [Eqs. (2)–(7)] into the simplified relations, Eqs. (8)–(12).

(i) From constraint (a) in Sect. II B, one may neglect the terms $R_{\text{diss}}(c,A_2)$ and $R_{\text{recomb}}(c,A)$ in Eqs. (2) and (3). Also in Eqs. (2) and (3), one can neglect terms involving $(SA)_1$ owing to the approximation in Eq. (16) and (17), specifically, that $S1$'s surface area is sufficiently smaller than $S2$'s to render its fluxes of $A$ and $A_2$ negligible to global cavity concentrations.

(ii) Using constraint (b), one can approximate the adsorption rate, $R_{\text{ads}}$ as $R_{\text{ads}}(i,A_j) \simeq (1/\sqrt{6\pi})n(c,A_j)v_{A_j}$.

(iii) Using constraint (d), one can approximate all surface desorption rates, $R_{\text{des}}$, as $R_{\text{des}}(i,A_j) \simeq n(i,A_j)/\tau_{\text{des}}(i,A_j)$.

(iv) Constraint (f) in conjunction with (e) and (a) allows one to assume surface species concentrations are in chemical equilibrium and, therefore, that Eqs. (4)–(7) can be condensed to two expressions—one for $S1$ and one for $S2$—each in the form of Eq. (14): $K(i) = n(i,A_2)/n^2(i,A)$. On surface 1, the surface concentrations may be taken to be at equilibrium because the rates of surface dissociation and recombination far exceed the adsorption and desorption rates. Surface 2—owing to its dominance of cavity inventories of $A$ and $A_2$—is privileged relative to $S1$ in that the $A/A_2$ influx ratio to $S2$ is virtually identical to its $A/A_2$ efflux ratio. (This must be so, otherwise the cavity volume species concentrations would be constantly changing rather than being in steady state, which has been the assumption and which must be the case eventually.) Therefore, a weaker

TABLE III. Summary of derived system parameters for starting parameters in Tables I and II for the cavity concentration $n(c,A_2) = 2 \times 10^{16}$ m$^{-3}$ and temperature $T = 1000$ K.

| | Surface 1 | Surface 2 |
|---|---|---|
| $n(i,A)$ (m$^{-2}$) | $8.8 \times 10^{16}$ | $4 \times 10^{12}$ |
| $n(i,A_2)$ (m$^{-2}$) | $4.2 \times 10^{9}$ | $3.2 \times 10^{15}$ |
| $\theta(i,A)$ | $8.8 \times 10^{-3}$ | $4 \times 10^{-7}$ |
| $\theta(i,A_2)$ | $4.2 \times 10^{-10}$ | $3.2 \times 10^{-4}$ |
| $\tau_{\mathrm{des}}(i,A)$ (s) | 0.012 | 2.9 |
| $\tau_{\mathrm{des}}(i,A_2)$ (s) | 4000 | $8.7 \times 10^{-4}$ |
| $\tau_{\mathrm{diss}}(i)$ (s) | $10^{-12}$ | $3.7 \times 10^{-3}$ |
| $\tau_{\mathrm{recomb}}(i)$ (s) | $10^{-5}$ | $2.3 \times 10^{-6}$ |
| $R_{\mathrm{des}}(i,A)$ (m$^{-2}$ s$^{-1}$) | $7.3 \times 10^{18}$ | $1.4 \times 10^{12}$ |
| $R_{\mathrm{des}}(i,A_2)$ (m$^{-2}$ s$^{-1}$) | $1.1 \times 10^{6}$ | $3.7 \times 10^{18}$ |
| $\dfrac{R_{\mathrm{des}}(i,A_2)}{R_{\mathrm{des}}(i,A)} \equiv \alpha$ | $1.4 \times 10^{-13}$ | $2.6 \times 10^{6}$ |



FIG. 1. Variation of surface and cavity species densities vs cavity density $n(c,A_2)$ for representative system. Model limits are indicated by dotted lines. Up arrows on the abscissa indicate limits for most viable cavity densities of operation.

condition for $S2$'s surface chemical equilibrium suffices: simply, that the transit time of $A$ or $A_2$ is short compared with the average surface desorption time of either species $[\tau_{\mathrm{trans}}(A_j) \ll \tau_{\mathrm{des}}(2,A_j)]$. If the second condition of (f) is met—$\tau_{\mathrm{des}} \gg \tau_{\mathrm{recomb}}, \tau_{\mathrm{diss}}$—the surface species may be treated as in dissociative-recombinative equilibrium [25]; in other words, the rate of $A_2$ dissociating on a surface is closely matched by the rate of $A$ atoms recombining there, that is, $R_{\mathrm{diss}}(i) \simeq R_{\mathrm{recomb}}(i)$. Species form the two-dimensional analog of the standard three-dimensional gas phase equilibrium with the exception that now the chemical nature of the surface helps determine their concentrations.

(v) In reducing Eqs. (4) and (5) to a single expression and in neglecting $A$ and $A_2$ fluxes from $S1$ in Eqs. (2) and (3), some information was lost, namely, that the number of $A$ atoms on $S1$ is conserved. Conservation of $A$ (summing $A$ and $A_2$ contributions) is embodied in Eq. (12).

## APPENDIX B: REPRESENTATIVE DSPG SYSTEM

Owing to the many independent variables specifying it—about two dozen in Tables I and II—complete multivariable analysis of a general DSPG system is intractable. In this appendix, it will be shown for one particular DSPG system that (a) with physically realistic parameters, a steady-state pressure difference, $\Delta P \gg \delta P_{\mathrm{rms}}$, is obtained and (b) the physical constraints of the model are self-consistent.

Let a cavity (scale length $L_{\mathrm{cav}} = 0.1$ m) be coupled to an "infinite" 1000 K heat bath. The surface area of $S1$ (scale length $L_{S1} = 10^{-3}$ m) is $10^{-9}$ times less than that of $S2$. (Let the cavity have a dendritic structure and let $S2$ be porous.) Other system parameters are given in Tables I and II. Derived system parameters are summarized in Table III. In Fig. 1 are plotted the various equilibrium surface and volume species densities versus volume density $n(c,A_2)$. These are calculated from simultaneous solution of Eqs. (8)–(12), given $n(c,A_2)$ as the independent variable. Simultaneous solution of the more general equilibrium relations, Eqs. (2)–(7), under the approximation of surface chemical equilibrium, render the same results as the simplified equations to within about 10%.
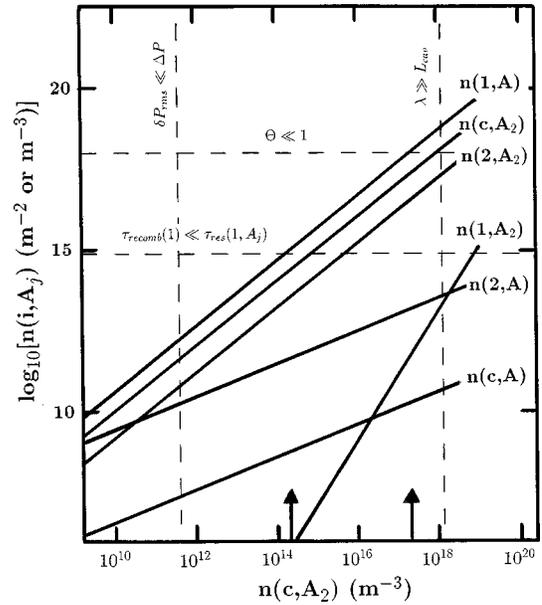
Several features in connection with this system and with Fig. 1 are noteworthy:

(a) As expected, each $n(i,A_j)$ increases linearly (logarithmically) with increasing $n(c,A_2)$.

(b) Species $A_2$ dominates surface 2 and cavity inventories while $A$ dominates surface 1.

(c) Inspection of Fig. 1 and Table III indicates that surfaces 1 and 2 display different desorption ratios for all values of $n(c,A_2)$. In particular, at $n(c,A_2) = 2 \times 10^{16}$ m$^{-3}$, one has $1.4 \times 10^{-13} = \alpha(1) \ll \alpha(2) = 2.6 \times 10^{6}$.

(d) The different desorption ratios occur simultaneously and in steady state in a single cavity.

(e) The volume density interval (bounded by the two up arrows on the abscissa in Fig. 1), $2 \times 10^{14} \leq n(c,A_2) \leq 2 \times 10^{17}$ m$^{-3}$, satisfies all the constraints and limits described in the main text and indicates the most viable region of operation for this system. The right limit line in Fig. 1 is set by the condition that $\lambda \gg L_{\mathrm{cav}}$. Here it is taken to be $\lambda = 10L_{\mathrm{cav}} \simeq 1$ m. The lower limit line is set by the condition that $\tau_{\mathrm{recomb}}(1) \ll \tau_{\mathrm{des}}(1,A)$. This puts a lower limit on $n(1,A)$. Here it is taken to be $10n(1,A) = 7.6 \times 10^{14}$ m$^{-2}$. The left limit line is set by the condition that the statistical pressure fluctuations, $\delta P_{\mathrm{rms}}$, over the scale length of the $S1$ patch be much less than the pressure difference, $\Delta P$. Here the limit is taken to be $\delta P_{\mathrm{rms}} \leq 10\Delta P$, rendering a lower limit density, $n(c,A_2) = 4 \times 10^{11}$ m$^{-3}$. The upper limit line is set by the condition that the surface coverage by any species be much less than 1 ML. Here it is taken to be $\theta = 0.1$, or $n(i,A_j) = 10^{18}$ m$^{-2}$. From these limits, it appears this system should display the DSPG effect over about three orders of magnitude in cavity gas density $[2 \times 10^{14} \leq n(c,A_2) \leq 2 \times 10^{17}$ m$^{-2}]$.

(f) The pressure difference $\Delta P$ should be in the range $8 \times 10^{-7} \leq \Delta P \leq 8 \times 10^{-4}$ Pa over the viable cavity density range (see above). This pressure is significant in the context of the DSPG; i.e., $\Delta P \gg \delta P_{\mathrm{rms}}$.

(g) It was verified numerically and analytically that the values of any parameter in Tables I and II could be varied—in some cases, up to several orders of magnitude from their table-stated values—and the DSPG effect would persist.

In summary, there appears to be a broad range of physical values over which the DSPG effect is viable.

### 1. Self-consistency

For this representative system, the DSPG model is self-consistent. (In other words, the physical parameters necessary for the validity of the model constraints are generated by the system itself.) Several model constraints do not have quantitative support, but must be accepted implicitly; they are constraints (b), (c), and (e) in Sec. II B. These, however, are commonly assumed in other surface chemical models and are defended here:

*Constraint (b):* For real surfaces, sticking coefficients, $s(i, A_j)$, range from near zero to near unity. Unity was chosen for convenience, however, it is easily shown that lesser values do not invalidate the principal results. As for the constraint of thermal equilibrium, if a species is in contact with a surface for more than a few surface vibrational periods (typically $\tau \gtrsim 10^{-12}$ sec), the species should achieve thermal equilibrium with the surface. Since the average residence times for any species for either $S1$ or $S2$ is at least $10^8$ times longer than the thermal equilibration time, it is reasonable to assume all species achieve thermal equilibrium with a surface and, therefore, leave in thermal equilibrium.

*Constraint (c):* The constraint that ''the only relevant surface processes are adsorption, desorption, dissociation, and recombination'' is defensible for its first-order, phenomenological descriptiveness of real systems. Ideally, many potentially interesting surface effects can be added, for instance, multidimensional molecule-surface potential energy surfaces, surface loading effects, tunneling, incorporation, absorption, surface defects, edge effects, side chemical reactions, activation energies of desorption, precursor states, and potential energies of mobility. These may add detail to the model, but do not necessarily preclude the effect.

*Constraint (e):* It has been shown theoretically and experimentally that surface species can be highly mobile in translation parallel to surfaces. Energy barriers impeding parallel transport are commonly 1/3 to 1/10 those values for perpendicular transport (desorption) and so, given the exponential thermal dependencies for surmounting barriers, it is reasonable for a species to be tightly bound in the direction perpendicular to a surface while being effectively free to move in the parallel direction [26].

The remaining constraints can be justified quantitatively on the basis of the derived systems properties. Constraints (a) and (d) have been verified already in the context of limit lines in Fig. 1. It was claimed that gas phase populations have little effect on the total cavity inventories of either species. Analysis indicates gas phase collisions, regardless of their products, cannot shift cavity inventories of either species by more than about one part in $10^6$ from those values obtained by entirely neglecting those collisions. Furthermore, any compositional changes caused by gas phase collisions are erased during the long surface residence times of both species. In fact, the cavity wall ($S2$) is the principal reservoir for both species. For instance, at the cavity concentration, $n(c, A_2) = 2 \times 10^{16}$ m$^{-3}$, the combined volume and surface loads of $A$ and $A_2$ are roughly $4 \times 10^{15}$ atoms and $3.2 \times 10^{18}$ molecules. The number fractions of $A$ atoms associated with $S1$: $S2$: cavity volume are $2.2 \times 10^{-5}$: $\sim 1$: $1.4 \times 10^{-9}$. For $A_2$ molecules the fractions are $1.3 \times 10^{-15}$: $\sim 1$: $6.3 \times 10^{-6}$. These ratios indicate $S2$ dominates cavity inventories of both species.

Surface 2 also dominates the fluxes of both species. In Sec. III, it was claimed that inequalities Eqs. (16) and (17) must be satisfied for $S2$ effluxes to greatly exceed $S1$ effluxes. From Tables I and III, it can be shown that $3.4 \times 10^{12} = R_{des}(2, A_2) / R_{des}(1, A_2) \gg (SA)_1 / (SA)_2 = 10^{-9}$, and $1.9 \times 10^{-7} = R_{des}(2, A) / R_{des}(1, A) \gg (SA)_1 / (SA)_2 = 10^{-9}$. Both inequalities are satisfied.

*Constraint (f):* The transit time for this system is roughly $\tau_{trans}(A_j) \sim L_{cav} / v_{A_j} \sim 10^{-4}$ sec. From Table III, it is evident that the desorption times for all species on both surfaces are much longer than $\tau_{trans}$, implying that $A$ and $A_2$ spend the vast majority of their time on surfaces rather than in the gas phase. Thus, for $S2$—with its cavity dominance of both species shown above—one may assume surface chemical equilibrium. On the other hand, for $S1$ with its influx and efflux being distinct from each other, it is also required that $\tau_{recomb}, \tau_{diss} \ll \tau_{des}$. Again, examining Table III and Fig. 1, this condition is met.

In summary, it has been shown that for one set of realistic physical and thermodynamic parameters, within a sealed cavity, $S1$ and $S2$ can simultaneously desorb different ratios of $A$ and $A_2$ in a steady-state fashion; and they can generate a steady-state, statistically significant pressure difference (and gradient). All model constraints were shown to be self-consistent and/or physically reasonable.

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[3] Care must be taken in evaluating Eqs. (4)–(7) since the equation pairs (4,5) and (6,7) are partial linear combinations. Direct simultaneous solution can erase the roles of $R_{recomb}(i)$ and $R_{diss}(i)$. This should be accounted for with ancillary relations, for instance, the $K(i)$ term, Eq. (14), to assure surface chemical equilibrium.

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[26] Note, however, that bound species may be constrained to particular quantum states and geometric orientations on the surface, thereby affecting collision processes (affecting, for instance, the values of many parameters in Table II).