Multi- and In-stabilities in gas partitioning between nanoporous materials and rubber balloons

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Abstract

In the two-balloon experiment, two rubber balloons are connected and allowed to exchange gas. Owing to the non-monotonic relationship between the radius of the balloon and the pressure of gas inside of it, the two-balloon system presents multi- and instabilities. Herein, we consider a two-adsorbent system, where two different adsorbents are allowed to exchange gas. We show that, for rigid adsorbents, the thermodynamic equilibrium state is unique. Then, we consider an adsorbent-balloon system, where an adsorbent exchanges gas with a rubber balloon. This system can exhibit multiple states at thermodynamic equilibrium—two (meta)stable and one unstable. The size of the balloon, pressure of gas in the balloon, and partitioning of gas between the adsorbent and the balloon differ among the equilibrium states. Temperature changes and the addition/removal of gas into/from the adsorbent-balloon system can induce catastrophe bifurcations and show hysteresis. Furthermore, the adsorbent-balloon system exhibits a critical temperature where, when approached from below, the discrepancy of balloon size between the two (meta)stable states decreases and, beyond, bistability
is impossible. Practically, our findings preclude multiple partitions of adsorbed gas in rigid mixed-linker metal-organic frameworks and may inspire new soft actuator and sensor designs.

Introduction

Nanoporous materials such as metal-organic frameworks (MOFs)\(^1\) exhibit permanent porosity and harbor large internal surface areas (\(>7000\ \text{m}^2/\text{g}\)).\(^2\) When immersed in gas, dispersive and electrostatic interactions between gas molecules and the walls of the pores enable nanoporous materials to achieve an adsorbed gas phase density greater than that of the bulk gas phase. As a consequence, nanoporous materials offer several engineering applications in gas storage,\(^3\) including storage of hydrogen\(^4\) and natural gas\(^5\) onboard vehicles for fuel and the safe sub-atmospheric storage of toxic gases used in semiconductor manufacturing.\(^6,7\)

MOFs are assembled modularly from metals or metal clusters as nodes and organic molecules as linkers.\(^1\) Mixed-linker MOFs\(^8\) are synthesized using two different organic molecules as linkers. Some mixed-linker MOFs harbor small spatial domains that display distinct surface chemistries\(^9,10\) and thus different affinities for a gas. An important question is whether, at thermodynamic equilibrium, a mixed-linker MOF harboring two distinct spatial domains can exhibit multiple stable states that differ in the partitioning of gas between the two domains. To address this question, we first study the conceptually equivalent two-adsorbent system in Fig. 1a, where a nanoporous material is allowed to exchange gas with another, different nanoporous material.

Many MOFs harbor flexible backbones and, triggered by the adsorption of gas molecules, contract or expand significantly.\(^11-13\) Co(bdp) boasts the highest deliverable capacity of methane for natural gas storage because it collapses and expels its residual gas at the desorption pressure.\(^14,15\) A rigid vessel is likely not suitable for containing a flexible material that significantly swells and contracts when gas is ad-/de-sorbed. As a substitute that allows expansion and contraction of the material, an elastic bladder may serve as the container of a
flexible material for adsorbed natural gas storage. However, the stress imposed on a flexible material by the elastic bladder is intimately coupled to the amount of gas adsorbed,\textsuperscript{14,16} coupling the design of the elastic bladder and the flexible nanoporous material. Herein, we investigate the thermodynamics of a related but simpler adsorbent-balloon system in Fig. 1b, where a rigid adsorbent can exchange gas with a rubber balloon. We determine whether the adsorbent-balloon system can exhibit multiple stable thermodynamic equilibria that differ in the gas pressure, size of the balloon, and partitioning of gas between the balloon and adsorbent. Unexpectedly, the catastrophe bifurcations we find in the adsorbent-balloon system may inspire new designs of soft actuators and sensors\textsuperscript{17} in robotics and medicine.\textsuperscript{18}

We find that the equilibrium thermodynamics of the two-adsorbent and adsorbent-balloon systems in Fig. 1 are closely related. Through thermodynamic modeling, we show that the two-adsorbent system cannot display multiple stable states at equilibrium when the adsorbents are rigid. However, when a flexible, breathing MOF exchanges gas with a rigid material, the two-adsorbent system can exhibit two (meta)stable states, differing in the pressure of gas in the system, the partitioning of gas between the two adsorbents, and the phase adopted by the flexible material. Moving on to the adsorbent-balloon system, we show it can exhibit three different states at thermodynamic equilibrium, two (meta)stable and one unstable. The pressure of gas in the balloon, radius of the balloon, and partitioning of gas between the adsorbent and the balloon differ among each equilibrium state. Furthermore, catastrophe bifurcations (instabilities) can occur upon adding or removing gas from the system, where a differential change in the amount of gas in the system induces a discontinuous change in the radius of the balloon. A similar catastrophe bifurcation occurs with temperature changes as a consequence of gas uptake in the adsorbent scaling nonlinearly with temperature. The Gibbs free energy surface governing the adsorbent-balloon system at thermodynamic equilibrium indicates that the catastrophe bifurcations result in heat released into the environment. Finally, we find the adsorbent-balloon system displays a critical temperature which, when approached from below, the discrepancy of balloon size between the two (meta)stable states
Figure 1: An adsorbent exchanging gas with another adsorbent and with a balloon. (a) Two connected vessels are each filled with a different porous material and allowed to exchange gas. (b) A vessel is filled with a porous material and allowed to exchange gas with a rubber balloon. A gas inlet line allows adjustment of the total number of moles of gas $N$ in each system.
Modeling the gas, adsorbent, and rubber balloon

We describe the gas, adsorbent, and rubber balloon membrane with the ideal gas law, Langmuir adsorption model, and Arruda-Boyce 8-chain hyperelastic constitutive model, respectively. Each of these models springs from a statistical mechanical treatment of a molecular-scale view. Our qualitative predictions in this study are predicated only on the shapes of curves; for this reason, we omitted scales on the axes on most of the plots in this article. We employ particular models for clarity, concreteness, and illustration. For full transparency of the parameters we used, a Jupyter Notebook with Julia code to fully reproduce all plots in this article is available on Github at github.com/SimonEnsemble/adsorbents_balloons_exchange_gas.

The Langmuir adsorption model

We model equilibrium gas adsorption in the porous material with the Langmuir adsorption equation:

$$N(P) = M \frac{KP}{1 + KP},$$

where $N$ is the amount of gas adsorbed, $P$ is the pressure of the bulk gas in equilibrium with the adsorbed phase, and $K$ is the Langmuir constant of the porous material. The Langmuir constant describes the affinity of the gas for the walls of the porous material and dominantly depends exponentially on inverse temperature. See Fig. S1b for a plot of the Langmuir adsorption curve and Sec. S1.2 for a statistical mechanical derivation and assumed characteristics of a Langmuirian material.
The Arruda-Boyce 8-chain hyperelastic constitutive model

We model the rubber balloon membrane with the Arruda-Boyce 8-chain model\textsuperscript{20,22} because it reasonably predicts the equibiaxial stress-strain relationship of rubber and springs from a statistical mechanical treatment of a molecular view of rubber. At the molecular level, rubber is an isotropic network of long, entangled, and cross-linked polymer chains.\textsuperscript{23}

Under the Arruda-Boyce 8-chain crystalline model of rubber, the polymer network of rubber is composed of cubic unit cells, each possessing eight identical polymer chains connected at a single node in the center, with the other ends connected to the corners. See Fig. S2b. Each of the 8 chains consists of $n$ monomers of length $b$ and is described by the freely jointed chain model,\textsuperscript{23,24} whose free energy we derive from statistical mechanics in Sec S1.3.1.

In the absence of stress, the average end-to-end length of each chain in the unit cell is $\sqrt{nb}$ (the polymer undergoes a random walk), and, via simple geometry, the average dimension of the unit cell is $\ell_0 = \frac{2}{\sqrt{3}}\sqrt{nb}$.

Relevant to inflating a rubber balloon, consider the 8-chain unit cell under equibiaxial tension with the principal stretch directions aligned with the $x$ and $y$ unit cell axes.\textsuperscript{20} As a result of symmetry, (i) the connection node interior to the unit cell remains in the center and (ii) each chain is stretched by an equivalent factor. Let $\lambda$ be the factor by which the unit cell is stretched from the resting configuration in the $x$ and $y$ directions (the stretch ratio). Treating rubber as incompressible— a good approximation for extensions up to 300%,\textsuperscript{23,25}— the average end-to-end vector of one of the chains is $\ell_0^2(\lambda, \lambda, \lambda^{-2})$ and thus the expected value of the end-to-end distance $x$ of each chain in the cell under equibiaxial tension is:

$$\langle x \rangle \approx \frac{1}{\sqrt{3n}}\sqrt{2\lambda^2 + \lambda^{-4}}.$$  \hspace{1cm} (2)

We now obtain the free energy of a spherical rubber balloon membrane whose radius and thickness in the absence of stress are $r_0$ and $z_0$, respectively. When the rubber balloon is inflated, under the thin walled-tank approximation,\textsuperscript{26} each infinitesimally small, rectangular
prism-shaped patch of the balloon membrane is under equibiaxial tension with the tensions tangential to the surface of the sphere. If $r$ is the radius of the inflated balloon and $\lambda$ is the stretch ratio under the equibiaxial tension, incompressibility of the membrane implies that $\lambda = r/r_0$. With $\rho$ the density of Arruda-Boyce polymer chains in the rubber comprising the membrane of the balloon, the free energy of the membrane of the inflated balloon is $4\pi r_0^2 z_0 \rho A_{FJC}$, where $A_{FJC} = A_{FJC}(\lambda)$ is the free energy of a freely jointed chain given by eqn. S12; the average end-to-end length $\langle x \rangle / (nb)$ of each identically stretched freely jointed chain comprising the Arruda-Boyce 8-chain unit cell membrane is given by eqn. 2, with $\lambda = r/r_0$.

The surface tension $\sigma$ of the balloon membrane is defined by how the free energy changes upon a differential increase in area of the membrane. Since the area of the membrane is $2 \cdot 4\pi (r_0 \lambda)^2$, the surface tension in terms of the stretch ratio is:

$$\sigma(\lambda) = \rho z_0 \frac{1}{4\lambda} \left( \frac{\partial A_{FJC}}{\partial \lambda} \right)_{n,T}.$$  \hspace{1cm} (3)

We compute the surface tension $\sigma = \sigma(r)$ of the rubber balloon membrane when it adopts a radius $r$ via eqn. 3 using autodifferentiation.\textsuperscript{27}

**Two adsorbents exchange gas**

See Fig. 1a for the two-adsorbent system. Two rigid pressure vessels are each filled with a different adsorbent and are connected to allow gas exchange. The number of gas molecules $N$, volume $V$, and temperature $T$ are held fixed. Without loss of generality, we take each compartment in Fig. 1a to contain one unit mass of adsorbent.

At thermodynamic equilibrium, the chemical potentials of the gas phase in the connection tube and the two adsorbed phases in the porous materials in vessels 1 and 2 are equal:

$$\mu_{\text{ads} 1} = \mu_{\text{tube}} = \mu_{\text{ads} 2}.$$  \hspace{1cm} (4)
The left- and right-most equalities imply that the amount of gas adsorbed in the porous materials follow their adsorption isotherms. Neglecting the gas in the connection tube, conservation of mass dictates:

\[ N_1(P) + N_2(P) = N, \quad (5) \]

with \( N_i(P) \) the adsorption isotherm of the porous material in vessel \( i \), written in terms of pressure \( P \) in the connection tube instead of chemical potential \( \mu \) using the ideal gas law.

We find the pressure \( P \) in the connection tube that satisfies eqn. 5 under different scenarios using a graphical approach inspired by Müller and Strehlow;\textsuperscript{28} see Fig. 2. The partitioning of gas between the two adsorbents follows.

![Graphical approach to identify the equilibrium state of the two-adsorbent system given by eqn. 5. The intersection of the curves \( N_1(P) \) and \( N - N_2(P) \) determine the equilibrium pressure of the gas in the connection tube. The black, dashed line shows \( N \), the total moles of gas in the system. The panels differ in what type of materials are considered in the compartments: (a) both adsorbents rigid and Langmuirian; (b) one adsorbent rigid and Langmuirian, the other possessing a 3D pore architecture permissive of a phase transition of the fluid inside its pores below the bulk saturation pressure, leading to a discontinuity in the adsorption isotherm; (c) one adsorbent rigid and Langmuirian, the other flexible and bistable, able to persist in a narrow-pore (np) or large-pore (lp) phase. Adsorption/desorption hysteresis is present due to the persistence of the material in a metastable state. The dashed line in \( N_1(P) \) delineates the global free energy minima from metastable states on each branch within the hysteresis loop. The star marks coexistence of (b) the gas and liquid phases of the fluid in the pores (c) the np and lp phases of the crystal. The ‘x’ indicates the equilibrium state is metastable.](image)
Gas exchange between two rigid Langmuirian adsorbents

We first take the two porous materials in Fig. 1a to be rigid and, for illustration, model their adsorption isotherms as Langmuirian (eqn. 1). The single solution identified by the graphical approach in Fig. 2(a) is stable because transferring $\delta N$ moles of gas from adsorbent 1 to adsorbent 2 results in a lower (higher) pressure exhibited by adsorbent 1 (2); a corrective response results.

The graphical approach in Fig. 2 is helpful for determining if multiple equilibrium states can possibly exist. Given the adsorption isotherms $N_i(P)$ are continuous, $\lim_{P \to 0} N_i(P) = 0$ (guaranteed by thermodynamics\textsuperscript{29}), and the adsorbents are together capable of holding $N$ moles of gas, the intermediate value theorem guarantees the existence of an equilibrium solution. If, in addition, the adsorption isotherms $N_i(P)$ are monotonic, the equilibrium solution is unique and stable.

For a rigid porous material, statistical mechanics guarantees that the adsorption isotherm is monotonically increasing with chemical potential, since:

$$
\frac{\partial^2 \log \Xi}{\partial (\beta \mu)^2} = \frac{\partial \langle N \rangle}{\partial (\beta \mu)} = \text{var}(N) \geq 0, \quad (6)
$$

where $\Xi = \Xi(\mu, V, T)$ is the grand-canonical partition function.\textsuperscript{23} This connection between fluctuations of the amount of gas adsorbed and the slope of the adsorption isotherm is not specific to the Langmuir model of adsorption. Thus, we conclude that the two-adsorbent system in Fig. 1a, where the adsorbents are rigid and display continuous adsorption isotherms, cannot exhibit multistability at thermodynamic equilibrium.

Involving pore condensation

If the adsorption isotherm of one of the rigid porous materials presents a discontinuity, one can see from the graphical approach in Fig. 2(b) that a solution to eqn. 5 may not appear to exist. A discontinuity in the adsorption isotherm can arise if the gas condenses in the pores of
a crystalline material. For example, MOF-5 possesses a three-dimensional pore architecture that is permissive of a true phase transition of a fluid below its bulk saturation pressure, as is shown to occur with benzene adsorption in MOF-5\textsuperscript{30} (adsorption isotherm in Ref.\textsuperscript{31}). In a case such as in Fig. 2(b), with the discontinuity arising from fluid condensing in the pores, conservation of mass in eqn. 5 would be satisfied by phase coexistence in the pores at the pressure at which the discontinuity occurs. Note the subtlety here that the grand potential for one of the compartments in Fig. 1a is necessarily analytic since we consider fixed $N$; thus the adsorption isotherm cannot present a true discontinuity at fixed $N$; instead, it will present a steep but finite slope.

**Involving flexible materials**

Now we relax the assumption that the porous material is rigid. Consider when one compartment in Fig. 1a contains a flexible porous crystal that, triggered by the adsorption of gas molecules, can contract or expand significantly.$^{11-13}$ Assume the compartment (i) does not adapt to the volume of the flexible material so as to retain void space that arises when the material contracts and (ii) possesses sufficient volume to accommodate the most expanded form of the material. Then, considering the entire compartment (porous material and void space) as the system, eqn. 6 still dictates that the number of molecules in the compartment must increase monotonically with chemical potential at thermodynamic equilibrium. Therefore, from the graphical view in Fig. 2, if the adsorption isotherms in the flexible materials are continuous, the two-adsorbent system exhibits a unique pressure at thermodynamic equilibrium also when flexible materials are involved.

We now show that, however, flexible materials persisting in a metastable state can introduce multiple equilibrium states in the dual-adsorbent system. In the case of breathing or gate-opening frameworks, the crystal structure undergoes a first-order structural transition, triggered by an increase in the chemical potential of the gas and associated with a change in volume of the crystal.$^{12}$ Such a transition introduces a discontinuity in the adsorption
isotherm concomitant with the abrupt contraction or expansion of the framework (subject to the proviso mentioned above in regard to thermodynamic discontinuities in a finite system). Moreover, hysteresis loops arise in the adsorption isotherms of breathing MOFs due to the persistence of a metastable crystalline phase; e.g., see xenon adsorption in MIL-53(Al).\textsuperscript{32} Fig. 2(c) shows, as a consequence of the hysteresis loop, two (meta)stable solutions can persist in the two-adsorbent system. In this illustration, the empty crystal is bistable, adopting either a narrow- or large-pore phase. Given that the narrow-pore phase of the empty host is more stable, the material persists in this phase when immersed in gas at low chemical potentials. At higher chemical potentials, the framework expands to the large-pore phase to accommodate more gas, which stabilizes the large-pore phase. See the work of Coudert et al.\textsuperscript{33} Because of adsorption/desorption hysteresis, Fig. 2(c) shows that the two-adsorbent system involving a breathing MOF can present two (meta)stable states that differ in the gas pressure, partitioning of gas between the two adsorbents, and the crystalline phase adopted by the breathing MOF. Depending on the slope of \(N_2(P)\), one or both of the equilibrium states are metastable. Another possible solution in Fig. 2(c) is the coexistence of the two structural phases of the crystal\textsuperscript{34} so as to adsorb gas to satisfy eqn. 5. Note that in Fig. 2(c) we have neglected the gas that may occupy the void space when the framework contracts.

Finally, we note a glaring exception to the monotonicity of adsorption isotherms with chemical potential, offered by metal-organic framework DUT-49.\textsuperscript{35} The adsorption of methane and \(n\)-butane in DUT-49 at 111 K and 298 K, respectively, abruptly drops as pressure is increased at c.a. 14 and 30 kPa, respectively.\textsuperscript{36} The expulsion of gas from the framework with a differential increase in chemical potential is concomitant with a dramatic contraction of the crystal structure,\textsuperscript{37} stabilized by more favorable guest-host interactions.\textsuperscript{38} The etiology of the drop in adsorption with an increase in chemical potential is, in addition to the volume change (\(V\) is fixed in eqn. 6), the DUT-49-methane system persists in a metastable state\textsuperscript{36,38} immediately below the pressure at which the drop in adsorption occurs; eqn. 6 assumes the system visits all of its possible microstates on the experimental time scale, which
is violated when the crystal is stuck in a metastable state. As Fig. S4 shows, owing to the non-monotonicity of the adsorption isotherm of methane in DUT-49, there could be three (meta)stable equilibrium states when DUT-49 is allowed to exchange gas with a Langmuirian material.

**An adsorbent and a rubber balloon exchange gas**

See Fig. 1b for the adsorbent-balloon system. A rigid vessel filled with an adsorbent is connected to a rubber balloon to allow gas exchange between the balloon and the adsorbent. Consider the adsorbent-balloon system with a fixed number of gas molecules \( N \), external pressure \( P_0 \), and temperature \( T \).

We seek to determine the pressure of gas in the balloon, size of the balloon, and partitioning of gas between the adsorbent and the balloon at thermodynamic equilibrium. Equating the chemical potentials of the bulk gas in the balloon and the adsorbed phase in the adsorbent, the amount of gas adsorbed follows the adsorption isotherm of the porous material, \( N_a(P) \), with \( P \) the pressure of gas in the balloon (related to chemical potential through an equation of state). We take \( N_a(P) \) to be a Langmuir adsorption isotherm (eqn. 1) for illustration. Mass conservation dictates:

\[
N_a(P) + N_b(P; P_0) = N, \tag{7}
\]

where \( N_b(P; P_0) \) is the amount of gas in the balloon as a function of pressure of the gas inside of it, \( P \)– the analogy to an adsorption isotherm for the balloon with an external pressure \( P_0 \) on the membrane. We employ a graphical approach to find the solution to eqn. 7 as in Fig. 2 after finding \( N_b(P; P_0) \), which we now seek.

In inflating a spherical rubber balloon with gas, the change in free energy of the rubber membrane of the balloon (related to surface tension) balances the \( PV \)-work (related to the
pressure jump across the membrane), leading to the Young-Laplace equation:

$$P - P_0 = \frac{4\sigma}{r},$$

(8)

with $P$ and $P_0$ the pressure of gas on the interior and exterior of the membrane, respectively, $r$ the radius of the balloon, and $\sigma = \sigma(r)$ the surface tension of membrane. For illustration, we describe $\sigma(r)$ by the Arruda-Boyce 8-chain model in eqn. 3. Using eqn. 8 in conjunction with the ideal gas law, Fig. 3a shows how the pressure of gas in a balloon, $P$, changes with the amount of gas in the balloon, $N_b$, as it is inflated; the color indicates the corresponding size of the balloon. Starting with an uninflated balloon, note that the pressure inside the balloon increases rapidly as gas is added because the balloon membrane is thick. At some point, the pressure in the balloon then decreases as gas is added because the membrane is stretched thin. As more gas is added, the pressure begins to increase again as the polymer chains in the balloon are extended into their non-Gaussian regime. See Fig. S5 for the explicit pressure-radius curve. Fig. 3a gives $N_b(P; P_0)$, which is multi-valued. We proceed to show that this non-monotonic relationship between the pressure and the amount of gas in a balloon brings about multiple (meta)stable states at thermodynamic equilibrium.

The graphical approach to solving eqn. 7 in Fig. 3b shows that three different states can exist at thermodynamic equilibrium, two (meta)stable (red disk and cross), one unstable (red circle). For the two (meta)stable states, transferring $\delta N > 0$ moles of gas from the balloon (adsorbent) to the adsorbent (balloon) results in an increase (decrease) in the pressure exhibited by the adsorbed phase and a decrease (increase) of gas pressure in the balloon, serving to correct the perturbation. The equilibrium solutions differ in the radius of the balloon, pressure of gas in the balloon, and partitioning of gas between the adsorbent and the balloon. In the metastable solution corresponding to the smaller balloon, the gas pressure is higher and more gas is adsorbed in the porous material compared to the large-balloon solution. Fig. 3c depicts the partitioning of gas between the adsorbent and balloon in the
small-, medium- (unstable), and large-balloon equilibrium states.

An implication of the adsorbent-balloon system in Fig. 1b in a bistable regime is that, e.g. if the balloon occupies the large-balloon state and we slowly squeeze it sufficiently to the small-balloon state, the balloon will not return to its original state spontaneously, but rather will persist in the small-balloon state. This hysteresis is illustrated in the bifurcation diagram in Fig. 4a that we discuss next.

The adsorbent-balloon system in Fig. 1b can display hysteresis and catastrophe bifurcations. Fig. 4a displays a bifurcation diagram with the total amount of gas $N$ in the system as the bifurcation parameter. For a regime of $N$, the system exhibits bistability, with the small- and large-balloon (meta)stable states and a medium-balloon unstable state. Systems with large (small) $N$ can exhibit only a large (small) balloon state. So, if we begin with a system with only a minute amount of gas, and then gradually add gas to the system, the system will proceed into the bistable regime in Fig. 4a, while persisting in the small-balloon state. After enough gas is added, however, the small-balloon solution disappears, and a catastrophe bifurcation occurs: the balloon abruptly expands upon adding a differential amount of gas to the system, jumping to the large-balloon branch in the bifurcation diagram. If $N$ is then decreased, the system proceeds through the bistable regime while persisting in the large-balloon state; a catastrophe bifurcation occurs as $N$ is decreased past the point where the large-balloon solution disappears and the balloon abruptly contracts as it jumps to the small-balloon branch on the bifurcation diagram. This hysteresis and catastrophe bifurcation can be seen by observing the intersections in Fig. 3b as the $N - N_b(P)$ curve is shifted up and down, corresponding to increasing and decreasing $N$, respectively.

A catastrophe bifurcation can also occur with temperature changes. Owing to the disparity between the linear scaling of surface tension and pressure in the balloon with temperature (see eqn. S12; these are entropic forces) and the dominantly exponential scaling with inverse temperature of the Langmuir constant $K$ of the adsorbent (see eqn. S5), the $N_a(P)$ curve in Fig. 3b is more sensitive to temperature changes. Thus, upon a differential increase (de-
Figure 3: Multi-stability in the adsorbent-balloon system in Fig. 1b. (a) The equilibrium relationship between the pressure of gas inside a balloon and the amount of gas it contains. The curve is colored according to the normalized radius of the balloon. (b) Graphical approach to solving eqn. 7. The pink curve is from panel (a), and the green curve is a Langmuir adsorption isotherm (eqn. 1). The stable (red disk), metastable (red ‘x’) and unstable (red circle) states are marked. (c) A bar plot depicting the partitioning of gas between the adsorbent and the balloon in the small, medium, and large balloon states from (b).
crease) in temperature, the small- (large-) balloon solution disappears, causing an abrupt expansion (contraction) of the balloon if the system begins in the small- (large-) balloon state. The catastrophe bifurcation with temperature is illustrated with the graphical approach in Fig. 4b. In each case, the unstable solution merges with the metastable state and disappears.

We show that one of the two stable equilibrium states in the bistable adsorbent-balloon system is metastable by plotting in Fig. 5a a heat map of the Gibbs free energy surface in the balloon size-gas partitioning plane (see Sec. S4 for derivation). In the middle panel, corresponding to an intermediate temperature, we see that a free energy barrier separates the small- and large-balloon states, which exhibit different minima of the free energy. Here, the small-balloon state is metastable. Given that the fluctuations in the macroscopic adsorbent-balloon system are highly unlikely to result in a spontaneous transition from the metastable state to the global free energy minimum on experimental time scales, both the small- and large-balloon states are practically stable. Also note that slowly squeezing a balloon in the large-balloon state can push the system into the small-balloon free energy basin and result in relaxation to the small-balloon state, consistent with hysteresis.

Comparison of the Gibbs free energy surfaces at different temperatures in Fig. 5a reveals that the catastrophe bifurcation with temperature changes are exothermic. Each catastrophe bifurcation corresponds to the disappearance of the metastable state as the unstable state—the saddle point in the Gibbs free energy—merges with the metastable state. Informally, a system in the metastable state then “rolls down the hill” to the global minimum in free energy, and heat is released. This also reinforces Fig. 4b by confirming that a system at higher and lower temperatures displays only one free energy basin, corresponding to the large- and small-balloon state, respectively.

Fig. 5b shows that there exists a critical temperature for the adsorbent-balloon system by displaying bifurcation diagrams as in Fig. 4a at multiple temperatures. Beyond the critical temperature, there cannot exist multiple stable states regardless of the amount of gas in
Figure 4: Hysteresis and catastrophe bifurcations displayed by the adsorbent-balloon system in Fig. 1b and induced by adding gas or changing the temperature. (a) Bifurcation diagram depicting equilibrium states (balloon size, pressure of gas in the balloon) of the adsorbent-balloon system with $N$ as the bifurcating parameter. Solid lines are stable states; dashed lines are unstable states. (b) Graphical approach to solving eqn. 7 (same as Fig. 3b) at different temperatures, depicted by color of the curves.
the system. Furthermore, as the temperature of the system below the critical temperature is increased, the discrepancy between the sizes of the balloons in the distinct (meta)stable small- and large-states decreases.

Discussion

Rubber and Rubber Balloons by Müller and Strehlow is an exposition on rubber balloons and their interesting properties, which motivated many of the ideas in this paper. Müller and Strehlow begin by introducing the two-balloon experiment, where two equivalent rubber balloons are inflated to different radii and connected to allow gas exchange. For a certain regime of initial radii, counter-intuitively, the smaller balloon expels much of its gas into the larger balloon, increasing the discrepancy in the two balloon radii. When two equivalent balloons of equal radii (and thus containing equal amounts of gas) are connected, for a certain regime of initial radii, symmetry breaking occurs, where one balloon decreases in size and empties much of its gas into the other balloon, whose radius consequently increases. That is, the equal radii equilibrium solution of the two-balloon system is unstable for a certain regime of initial [equal] radii. The behavior of the two-balloon system is reminiscent of two connected soap bubbles, but an important distinction is that the surface tension of a balloon is a function of its radius. The counter-intuitive behavior and instability of the two-balloon system stem from the non-monotonic relationship between the gas pressure in a balloon and its radius (See Fig. S5.)

Motivated by the two-balloon experiment, we first considered the two-adsorbent system in Fig. 1a, where two different porous materials are allowed to exchange gas. We determined that, when the two adsorbents are rigid, there exists a unique and stable state at thermodynamic equilibrium. This result sheds light on gas adsorption in a rigid, mixed-linker MOF crystal comprised of two spatial domains displaying distinct surface chemistries and thus different affinities for a gas. Conceptually, the two spatial domains exchanging gas
Figure 5: Gibbs free energy surface and critical temperature. (a) A heatmap depicting the Gibbs free energy $G$ in the $(N_a/N, r/r_0)$ plane. The red ball, ‘x’, and circle correspond to the stable, metastable, and unstable, respectively, equilibrium solutions at lower [left], intermediate [middle], and higher [right] temperatures. $N$ is the same in each panel. (b) A series of bifurcation diagrams for the balloon size ($r/r_0$) with $N$ the bifurcation parameter, as in the left panel of Fig. 4a, are depicted at different temperatures $T$. Systems above the critical temperature $T_c$ (gray curves) cannot exhibit bistability regardless of the amount of gas $N$ in the system. The discrepancy in size between the small- (green) and large-balloon (red) states decreases as the critical temperature is approached from below.
are represented by the two-adsorbent system, with each domain of the mixed-linker MOF possessing its own distinct adsorption isotherm equation owing to the distinct functional groups decorating the walls of the pores within the two domains. Our thermodynamic analysis indicated that there exists a unique partitioning of gas between the two spatial domains of a rigid, mixed-linker MOF. Interestingly, when a bistable, breathing MOF is allowed to exchange gas with a rigid adsorbent, we found there can be multiple (meta)stable states at thermodynamic equilibrium that differ in the gas pressure, partitioning of gas between the two adsorbents, and crystalline phase adopted by the flexible material.

We next considered when an adsorbent and a balloon can exchange gas. See Fig. 1b. We found that the adsorbent-balloon system can exhibit two (meta)stable states at thermodynamic equilibrium. Among the two (meta)stable states, the pressure of gas in the balloon, size of the balloon, and partitioning of gas between the adsorbent in the balloon differ. Moreover, we showed that hysteresis and catastrophe bifurcations can occur upon changes in temperature or addition/removal of gas into/from the system. Clearly from Fig. 3b, the non-monotonic pressure-radius curve of a balloon is also the etiology behind our balloon-adsorbent system exhibiting two (meta)stable states at thermodynamic equilibrium and displaying hysteresis and catastrophe bifurcations.

The catastrophe bifurcations with temperature changes and addition/removal of gas in the adsorbent-balloon system may inspire new designs of actuators and sensors, where a small change in temperature or amount of gas in the system can induce a large, discontinuous change in the size of an elastic membrane. Such “soft actuators” are sought in robotics and medicine.

Our Gibbs free energy heat maps in Fig. 5a reveal that the adsorbent-balloon system bears some semblance to vapor-liquid equilibrium in that it displays bistability with two different fluid densities in the balloon. Moreover, the adsorbent-balloon system exhibits a critical temperature above which bistability is not possible and, when approached from below, the densities of gas in the small- and large-balloon states converge. However, an
analogy with vapor-liquid coexistence is lacking.

We held the number of gas molecules $N$ constant in our analyses for both the two-adsorbent and adsorbent balloon systems to determine the equilibrium partitioning of gas between the two subsystems. Alternatively, we could have considered fixed chemical potential $\mu$. In this case, the problem becomes simpler because the two subsystems are now decoupled: the balloon and adsorbent(s) behave independently as both are connected to an infinite gas reservoir with chemical potential $\mu$.

We hope our theoretical predictions motivate an experiment where an adsorbent and a balloon are allowed to exchange gas to demonstrate multi-stability and the catastrophe bifurcations that we predict to occur when changing the temperature and amount of gas in the system. Our model can be used to guide the balloon and adsorbent properties required for bistability.

Acknowledgement

C.M.S. thanks the School of Chemical, Biological, and Environmental Engineering at Oregon State University for start-up funds.

Supplementary Information

A Jupyter Notebook with Julia$^{21}$ code to fully reproduce all plots in this article is available on Github at github.com/SimonEnsemble/adsorbents_balloons_exchange_gas. A Supplementary Information document is also available.

References


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