Two rubber balloons: Phase diagram of air transfer

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Two identical rubber balloons are partially inflated with air (to different extent) and connected by a hose with a valve. It is found that depending on initial balloon volumes, when the valve is opened the air will flow either from the larger (fuller) balloon to the smaller (emptier) balloon, or from the smaller balloon to the larger one. The phenomenon is explained in terms of the nonideal rubber elasticity of balloons. The full phase diagram for the air flow dynamics is constructed.

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I. INTRODUCTION

Consider two identical rubber balloons, the same ones as used at children’s parties, filled with air and connected by a hose with a valve. For simplicity, we shall approximate the balloons by spheres. Suppose that the larger balloon, the one that has been inflated more, has radius $R^b$ and contains $n_b$ moles of air, while the smaller one has radius $R^s$ and contains $n_s$ moles of air. When the valve is opened which balloon is going to grow and which will shrink? It seems almost obvious that the larger balloon should shrink, while the smaller one should grow. This, however, is not what is often found. For some balloon sizes the air flows from the larger balloon to the smaller one. The phenomenon is explained in terms of the nonideal rubber elasticity of balloons. The full phase diagram for the air flow dynamics is constructed.

II. THERMODYNAMICS

When the valve of the hose connecting the two balloons is opened, the direction of air flow is determined by the two laws of thermodynamics [1]. Suppose that $dn = -dn_b = dn_s$, moles of air are transferred from the bigger balloon to the smaller one. The work needed to accomplish this is determined by the first law of thermodynamics,

$$dW = TdS_0 + \sum_{i=b,s} (dE_i + dE'_i - TdS_i - TdS'_i + P_idV_i),$$  

where $S_0$, $P_0$, and $T$ are the environment entropy, pressure, and temperature; $E_i$, $P_i$, and $V_i$ are the internal energy, pressure, and volume of the gas inside the two balloons $i = b, s$; and $dE'_i$ is the internal energy of the balloon rubber membranes. The second law of thermodynamics requires that

$$dS_0 + dS_b + dS_s + dS'_b + dS'_s \geq 0,$$  

where $S_i$ and $S'_i$ are the entropy of gas and of the rubber membrane of balloon $i$.

Since the transfer of $dn$ moles of gas between the two balloons with finite pressure difference is an irreversible process, the total entropy of the universe will increase. It follows that the work necessary for the transfer is bounded from below by

$$dW > \sum_{i=b,s} (dE_i + dE'_i - TdS_i - TdS'_i + P_idV_i).$$  

From thermodynamics

$$dE_i = TdS_i - P_idV_i + \mu_idn_i,$$  

and

$$dE'_i = TdS'_i - P_idV'_i + \sigma_idA_i,$$  

where $V'_i$ is the volume of rubber, $\sigma_i$ is the surface tension, $A_i$ is the surface area, and $\mu_i$ is the chemical potential of gas inside the balloon $i$.

As a leading order approximation we can consider rubber to be incompressible, so that $dV'_i = 0$. Substituting Eqs. (4) and (5) into Eq. (3), we obtain

$$dW > \sum_{i=b,s} [(P_0 - P_i)dV_i + \sigma_idA_i + \mu_idn_i].$$  

For a spherical balloon, the variations in the volume and in the surface area are related by

$$\frac{dV_i}{dA_i} = \frac{R_i}{2},$$  

while the difference between the internal and the external pressures is governed by the law of Laplace [1],

$$P_i - P_0 = \frac{2\sigma}{R_i}.$$  

Substituting Eqs. (7) and (8) into Eq. (6), the amount of work necessary to accomplish the transfer of air is

$$dW > (\mu_s - \mu_b)dn.$$

For a gas at fixed temperature, the Gibbs-Duhem equation [2] is

$$-V_idP_i + n_id\mu_i = 0,$$

so that

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Using the ideal gas equation of state and integrating, the chemical potential inside each balloon is found to be

$$\frac{\partial \mu_i}{\partial P_i} = \frac{V_i}{n_i}. \quad (11)$$

Using the ideal gas equation of state and integrating, the chemical potential inside each balloon is found to be

$$\mu_i = \mu_0 + RT \ln \left( \frac{P_i}{P_0} \right), \quad (12)$$

where $\mu_0$ is the reference chemical potential at atmospheric pressure. Inserting Eq. (12) into Eq. (9), the amount of work necessary to transfer $dn$ moles of gas from the larger balloon to the smaller one is

$$dW > RT \ln \left( \frac{P_b}{P_i} \right) dn. \quad (13)$$

Transfer of gas will occur spontaneously if it does not require any external work, $dW=0$. For the specific case of two interconnected balloons this will be the case if the flow of air is from the balloon with high internal pressure to the one with low internal pressure. Furthermore, since the thermodynamics requires that $\partial \mu / \partial P > 0$, see Eq. (11), this conclusion holds for nonideal gases as well.

Although the calculation was performed for spherical balloons, it is evident that the conclusion concerning the direction of air flow, Eqs. (9) and (13), does not depend on the specific balloon shape. On the other hand, if the same balloons are filled with a heavy gas and are placed at different heights in the gravitational field, the flow of air will no longer be governed simply by the difference in internal pressure between the two balloons. Nevertheless, while Eq. (13) will lose its validity, Eq. (9) will remain correct; however, the chemical potential of gas will have to include a gravitational contribution as well.

III. RUBBER ELASTICITY

As air enters into the balloon, its rubber membrane stretches and becomes tense. The Helmholtz free energy of a rubber sheet is

$$F = E - TS. \quad (14)$$

If the sheet is subjected to a stress $\sigma$, its internal energy $E$ will vary in accordance with Eq. (5), and its Helmholtz free energy as

$$dF = dE - Ts - SdT = -PdV - SdT + \sigma dA. \quad (15)$$

The surface tension of the sheet is then

$$\sigma = \frac{\partial F}{\partial A} \bigg|_{V,T} - T \frac{\partial S}{\partial A} \bigg|_{V,T}. \quad (16)$$

It is an experimental fact [3] that up to fairly large extensions the internal energy of a rubber sheet is independent of its area.

This equation should be compared to a similar equation for the ideal gas—the internal energy of an ideal gas is independent of the volume that it occupies. Clearly, this is not correct for real gases, but serves as a very good approximation for a gas at low density. Similarly, Eq. (17) holds only for “ideal” rubber.

The Flory theory [3] allows us to calculate the change in entropy of an elastic object during a deformation. Suppose that the rubber sheet has dimensions $L_x$, $L_y$, and $L_z$ and that after the deformation the new dimensions are $\lambda_xL_x$, $\lambda_yL_y$, and $\lambda_zL_z$, then

$$\Delta S = -k [\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3 - \ln(\lambda_x\lambda_y\lambda_z)], \quad (18)$$

where $k$ is a constant related to the number of chains and the topological structure of the polymer network. If rubber is subjected to a not very high stress it is reasonable to assume that it is incompressible, so that $\lambda_x\lambda_y\lambda_z=1$. This means that for a uniform isotropic stress in the $x$-$y$ plane, $\lambda_x=\lambda_y=\lambda$ and $\lambda_z=1/\lambda^2$. Equation (18) then simplifies to

$$\Delta S = -k \left[ \frac{2A}{A_0} + \frac{A_0^2}{A^2} - 3 \right], \quad (19)$$

where $A_0$ is the surface area prior to the deformation and $A$ is the final surface area. It is important to note that a deformation of an elastic body results in a decrease of its entropy. Microscopically, this is a consequence of the reduction of the conformational volume accessible to a stretched polymer. Substituting Eq. (19) into Eq. (16), the surface tension of a rubber sheet is

$$\sigma = \kappa \left[ 1 - \frac{A_0^3}{A^3} \right], \quad (20)$$

where $\kappa=2kT/A_0$.

We expect Eq. (20) to work reasonably well up to extensions on the order of 100%. If the balloon is inflated beyond this “ideal” limit, deviations are to be expected. In general then, the stress-strain relation for a rubber balloon of radius $R$ can be written as

$$\sigma(R, R_0) = \kappa \left[ 1 - \frac{R_0^3}{R^3} \right] f \left( \frac{R}{R^*} \right), \quad (21)$$

where $R_0$ is the balloon radius prior to inflation, and the scaling function $f(x)$ governs the crossover from the ideal rubber regime to the nonideal one. The scale $R^*$ specifies the balloon size at which its rubber starts to behave nonideally. Here we use the simplest form of the crossover function,

$$f(x) = \begin{cases} 
1 & \text{for } 0 \leq x \leq 1, \\
A(x-1)\alpha + 1 & \text{for } x > 1,
\end{cases} \quad (22)$$

where $A>0$ and $\alpha>1$. Note that the function $f(x)$ is continuous and differentiable everywhere.
Transfer of $dn$ moles of air from the bigger balloon to the smaller one will occur spontaneously if the pressure inside the bigger balloon is larger than the pressure inside the smaller balloon. To simplify the notation, let us measure all the lengths in units of $R_0$ and define $R_s = u R_b$ with $h \frac{1}{R_b} \leq u \leq 1$. Using the law of Laplace,\begin{equation}
g(u; R^b, R^s, A) = P_b - P_s = \frac{2\sigma(R^b)}{R^b} - \frac{2\sigma(u R^b)}{u R^b}.
\end{equation}
If $g > 0$, once the valve is open there will be a spontaneous transfer of gas from the larger balloon to the smaller one. On the other hand, if $g < 0$ the transfer will proceed in the opposite direction. From Eqs. (21) and (22) we see that $g(1; R^b, R^s, A)=0$ while $\lim_{u \to 1/R^b} g(u; R^b, R^s, A) = \frac{2\sigma(R^b)}{R^b} > 0$. Therefore, unless the function $g$ has a zero on the interval $\{1/R^b \leq u \leq 1\}$ the larger balloon will always shrink, passing its air to the smaller balloon. Indeed for a given $f(x)$, we find that if $R^s < R^*_m$ then $g > 0$ for all $\{1/R^b \leq u \leq 1\}$, and the larger balloon always inflates the smaller one, see Fig. 1. The maximum value of the crossover scale $R^*_m$ and the balloon size $R^b$ for which this behavior occurs is determined by the set of equations\begin{equation}
g'(1; R^b_m, R^s, A) = 0
\end{equation}
and\begin{equation}
g''(1; R^b_m, R^s, A) = 0,
\end{equation}
where the prime denotes differentiation with respect to $u$.

We now distinguish two cases: $1 < \alpha < 2$ and $\alpha \geq 2$. For $\alpha \geq 2$ and $R^* > R^*_m$, the equation
\begin{equation}
g'(1; R^b_m, R^s, A) = 0
\end{equation}
has two roots $R^b_1$ and $R^b_2$ and a new phase in which small balloons inflate the larger ones appears, see Fig. 2. This phase terminates at a critical point, beyond which a large balloon with size $R^b > R^c$ will inflate any smaller balloon. For a given crossover function and crossover scale $R^*$, the

FIG. 1. Phase diagram for $R^* < R^*_m$. The 45° line is $R^b = R^s$. Arrow shows the direction of the air flux. The big balloon always inflates the smaller one.

FIG. 2. Phase diagrams for $R^* > R^*_m$. There are two distinct regimes, separated by a phase boundary terminating at a critical point, beyond which a large balloon will inflate any smaller balloon.

FIG. 3. Phase diagram for the ideal rubber balloons, $R^* \to \infty$.

FIG. 4. The shaded region indicates the parameters for which the topology of the phase diagram is the one shown in Figs. 5 and 6. Outside the shaded region the topology is the one presented in Figs. 1–3. As $\alpha \to 2$ the shaded area shrinks to zero.
location of the critical point is determined by the set of equations

\[ g(u_c; R^b_c, R^*, A) = 0, \]  

and

\[ g'(u_c; R^b_c, R^*, A) = 0. \]  

As the crossover scale grows, so do the values of \( R^b_c \) and \( R^* \). For \( R^* > 1 \),

\[ R^b_2 = aR^*, \]  

where \( a \) is the root of equation,

\[ a = \frac{A(a - 1)^a + 1}{Aa(a - 1)^{a-1}}. \]  

If the crossover scale goes to infinity, \( R^* \to \infty \), so that balloon rubber always behaves ideally, then \( R^b_2 \to \infty \) and \( R^c_1 \to \infty \). In this limit the phase diagram assumes the topology presented in Fig. 3.

For \( 1 < \alpha < 2 \), the phase diagram becomes even more interesting. For \( A \) and \( R^* \) inside the shaded area of Fig. 4, Eq. (27) has four solutions \( R_1^b, R_2^b, R_3^b \), and \( R_4^b \), and the possible topologies of the phase diagram are shown in Figs. 5 and 6. As the boundary of the shaded region is approached from inside, one of the phases shrinks and disappears and the phase diagram assumes the topology of Fig. 2. Outside the shaded region, the only possible topologies are the ones presented in Figs. 1–3.

The topological change from Fig. 5 to Fig. 6 occurs as \( R_3^b \to R_1^b \). As \( \alpha \to 2 \), the shaded area in Fig. 4 shrinks to zero and the topology of the phase diagram reduces to the one presented in Fig. 2.

**IV. CONCLUSION**

We have explored the thermodynamics of air transfer between two partially inflated rubber balloons. Surprisingly, for such an apparently simple system a very rich phase diagram governing the air transfer between the two balloons is obtained. We find that depending on the elasticity of balloon rubber and the initial balloon sizes, the air can flow either from the larger balloon to the smaller one, or vice versa. The topology of the phase diagram is controlled by the crossover function which characterizes the deviation of balloon rubber from the ideal Flory behavior.

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