Osmosis at constant volume. Negative pressure

Paško Županović,1 Domagoj Kučić,1 Milan Brumen,2 Alojz Fajmut,2 and Davor Juretić1

1 University of Split, Faculty of Science
Teslina 12, 21000 Split, Croatia
2 Faculty of Natural Science and Mathematics, Faculty of Medicine and Faculty of Health Sciences, Maribor, and Jožef Stefan Institute, Ljubljana, Slovenia

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A thermodynamic state of solvent and solution separated with an elastic semipermeable membrane, in the box with a fixed volume, is considered. It is shown that the minimum of the free energy is accompanied by the compression of the solution and tension of the solvent caused by the transfer of solvent molecules into compartment with solution. The tensile state of the solvent is described in terms of negative pressure. It is found that the negative pressure as well as compression pressure is of the order of osmotic pressure given by van’t Hoff equation. It is proposed that this mechanism could be responsible for the water uptake in tall trees.

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I. INTRODUCTION

The water, and generally liquids, is hardly compressed if the corresponding state is not too close to critical point. The usual values for bulk modulus, inverse compressibility, of liquids is of the order of \( GPa \approx 10^4P_0 \), where \( P_0 \) is the standard atmospheric pressure. On the other hand if the liquid is exposed to the tension one would expect, following standard thermodynamic books [1, 2, 3], that the tension equal to the difference between ambient pressure and pressure of saturated vapour at given temperature would be enough to detach the piston from the column of water. It is hard to believe that there is such discontinuity in the compressibility. Indeed experiments show that column of the water in the cylinder closed with a piston behaves like a solid adhesively bind to the inner surface of the cylinder and piston. One needs to apply the 0.13 GPa in order to break the water column, under the standard conditions. We used to say that the liquid under a tension is under a negative pressure.

The state of the liquid under negative pressure is metastable. The vapour bubbles generated by fluctuations, either on the contact surface between fluid and container or within fluid [4], are the seed of the new phase in which the vapour and liquid coexist. However if bubbles do not achieve a critical radius the increase of the pressure within it, due to the surface tension, will convert them back into the liquid. Radius of a vapour bubble is statistical value and tensile liquid after some time turns into stable phase of the coexisting liquid and vapour. The higher tension is applied to liquid the shorter lasts metastable state [5]. Once the tensile liquid turns into stable phase of coexisting liquid and vapour the pressure necessary to expand (or compress) system is equal to the difference between ambient pressure and pressure of saturated vapour.

Liquids under a negative pressure are the interesting problem for along period of time [5, 6, 7, 8, 9]. The state of negative pressure has been found in pure liquid systems [3, 4] and liquid-liquid systems [10, 11]. The aim of this paper is to show that osmosis between solvent and solution in compartments of the box with a constant volume leads to the state of negative pressure in compartment with solvent. Expanding the free energy of the solvent as the function of the intermolecular distances the dependence of the negative pressure on the molar concentration of solute and volumes of the compartments is found.
II. OSMOSIS

Osmosis is the process of the diffusion of a solvent into solution through semipermeable membrane.

The standard definition of the osmotic pressure relies on the osmosis at constant pressure shown on Fig. 1. Osmotic pressure is given by the van’t Hoff’s law [12, 13] and it is equal to the pressure of the free gas that has the same molar concentration as solute,

$$\pi = \frac{n_s}{V}RT.$$  

(1)

Here $n_s/V$ is the molar concentration of solute, $R$ is the gas constant and $T$ is absolute temperature.

![FIG. 1: Osmosis under constant pressure](image)

III. OSMOSIS AT CONSTANT VOLUME. NEGATIVE PRESSURE

We define a distance between molecules as a third root of the inverse value of concentration,

$$r = \sqrt[3]{\frac{V}{N}}.$$  

(2)

The distance between solvent molecules in the osmosis under fixed pressure is equal the corresponding equilibrium value $r_e$ in the pure solvent (see Figs. 1 and 2b). We encounter a different situation in the case of the osmosis at constant volume. Transition of the solvent molecules from left to right compartment is accompanied by the decrease and increase of the distances between solvent molecules in right and left compartment (see Figs. 2b and 2c), respectively.

Increase of the concentration of solute leads the decrease of the pressure in left compartment. At some critical value of concentration of solute the pressure falls to zero. Further increase in concentration lead to the tensile state. It is usually described as the state of the negative pressure.

Due to the presence of solute in right compartment small number of molecules crosses the membrane deforming it. Accordance to La Chatellier-Brown principle deformation of membrane increases the volume of the right compartment and decreases the volume of left compartment (Fig. 2c) in order to restore the mechanical equilibrium among them. The result is a membrane under tension compressing solution in the right and expanding the solvent in the left compartment, respectively. In the terms of the standard intermolecular force (Fig. 2d) the intermolecular distance between molecules in left and right compartments are $r_1 > r_e$ and $r_2 < r_e$, leading to the attractive and repulsive force among molecules in solvent and solution, respectively.
For the moment we consider box with pure solvent in both compartment (Fig. 2b). We calculate the change of the free energies of solvents in compartments, accompanied with a transfer of small number of molecules from one (left) to another (right) compartment, as a function of intermolecular distance. Due to the small compressibility of liquids this difference can be described by Taylor expansion of free energies of the systems in both compartments up to the second order in the change of the distance between molecules.

The expansion of free energy of the pure solvent in \( i \) –th compartment gives,

\[
\mathcal{F}_i(r_i) = \mathcal{F}_i(r_e) + \frac{\partial \mathcal{F}_i}{\partial r_i} \bigg|_{r_i=r_e} (r_i - r_e) + \frac{1}{2} \frac{\partial^2 \mathcal{F}_i}{\partial r_i^2} \bigg|_{r_i=r_e} (r_i - r_e)^2. \tag{3}
\]

Using the definition of the distance between molecules \( \eqref{distance} \) this equation becomes

\[
\Delta \mathcal{F}_i(r_i) = 3V_i p_i \left( \frac{r_i}{r_e} - 1 \right) + \frac{1}{2} \left[ \frac{9V_i}{\kappa} + 6V_i p_i \right] \left( \frac{r_i}{r_e} - 1 \right)^2. \tag{4}
\]

Here

\[
p_i = -\frac{\partial \mathcal{F}_i}{\partial V_i}, \tag{5}
\]

is the pressure in the \(-i\)th compartment, and

\[
\kappa = -\frac{1}{V_i} \frac{\partial V_i}{\partial p_i} \tag{6}
\]

is compressibility.
The transfer of molecules is accompanied with the change of the volume of compartments. The distance between molecules, the number of transferred molecules and the change of the volume are related by equation,

\[ V_i + \Delta V_i = (N_i + \Delta N_i) r_i^3 \]

Using Eq. (2) we get

\[ r_e \sqrt{1 + \frac{\Delta V_i}{V_i}} = r_i \sqrt{1 + \frac{\Delta N_i}{N_i}}. \]

Due to the small compressibility of liquid \( \Delta V_i / V_i \) \& \( \delta N_i / N_i \ll 1 \) linearization of above equation gives,

\[ \frac{\Delta V_i}{V_i} = 3 \frac{r_i - r_e}{r_e} + \frac{\Delta N_i}{N_i}. \]

The compressibility reads

\[ \kappa = -\frac{1}{V_i} \frac{\Delta V_{i,eff}}{p_i - p}, \]

where

\[ \Delta V_{i,eff} = (N_i + \Delta N_i) (r_i^3 - r_e^3), \]

and \( p_i \) is the pressure in the compartment. By means of (9) compressibility becomes

\[ \kappa = \left(1 + \frac{\Delta V_i}{V_i}\right) \frac{\left( \frac{r_e}{r_i} \right)^3 - 1}{p_i - p}. \]

Keeping only linear term in \( r_e - r_i \) we get

\[ \kappa = 3 \frac{r_e - r_i}{r_i(p_i - p)} \quad p_i > p \quad r_i < r_e \]

\[ p_i < p \quad r_i > r_e. \]

On the other hand the change of the pressure is a function of the change of volume. In linear approximation, taking into account that positive change of the volume leads to the increase of the pressure, we write

\[ p_i - p = c \frac{\Delta V_i}{V_i}. \]

Finally, by means of (11,13,14) the change of the free energy of the pure solvent due to the transfer of the transfer of the molecules from the left to right compartment in terms of change of volumes is

\[ \Delta F_w = -p \kappa c (\Delta V_1 + \Delta V_2) + \frac{kc^2}{2} \left( \frac{\Delta V_1^2}{V_1} + \frac{\Delta V_2^2}{V_2} \right). \]

Due to the fixed volume of the box \( \Delta V_1 + \Delta V_2 = 0 \). Putting \( \Delta V = \Delta V_2 = -\Delta V_1 \) we get

\[ \Delta F_w = \frac{kc^2}{2} \Delta V^2 \left( \frac{1}{V_1} + \frac{1}{V_2} \right). \]

As one has expected the minimum of the free energy coincides with zero change of the compartments’ volumes leading to \( r_e \) distance between molecules.

We now consider similar system with small box filled with solute in the right compartment (Fig.2b). The leak of the solute (Fig.2b) into right compartment modifies internal energy and entropy of the system. We assume that interaction between solvent molecules and solute ones are similar so we discard the change of the internal energy due to the mixing solvent and solute. In other words solute-solvent, solvent-solvent, and solute-solute interactions are taken to be equivalent. However we can not ignore the change of entropy due to the space delocalisation of the solvent. We use the free gas expression for entropy to describe the change of configuration entropy the system due to the solute diffusion from small box in upper right corner into right compartment (see Figs. 2b and 2c).
\[ S_s = n_s R \ln(V_2 + \Delta V) \approx nR \ln V_2 + n_s R \frac{\Delta V}{V_2}. \]  

(17)

The total free energy \( F = F_{w0} + \Delta F_w - T S_s \), where \( F_{w0} \) is the equilibrium free energy of the pure solvent in both compartments, reads

\[ F = F_{w0} + \frac{\kappa c^2}{2} \left( \frac{1}{V_1} + \frac{1}{V_2} \right) \Delta V^2 - nRT \frac{\Delta V}{V_2} \]

(18)

The minimum of the free energy (\( \partial F/\partial \Delta V = 0 \)) determines equilibrium change of the volume,

\[ \Delta V = n_s RT \frac{V_i}{\kappa c^2 (V_1 + V_2)} \]

(19)

The pressures due to the osmosis are

\[ p_i = p + \Pi_i, \]

(20)

where

\[ \Pi_i = n_s RT \frac{V_i}{\kappa c V_i (V_1 + V_2)} \frac{\Delta V_i}{\Delta V} \]

(21)

If effective change compartment volume with solvent is close to the negative value of change of the volume of the compartment

\[ \Delta V_{ieff} \approx -\Delta V_i \]

(22)

then

\[ c \approx \frac{1}{\kappa}, \]

(23)

and

\[ \Pi_i \approx n_s RT \frac{V_i}{V_i (V_1 + V_2)} \frac{\Delta V_i}{\Delta V} \]

(24)

The pressure difference between compartments is

\[ \Pi = \Pi_2 - \Pi_1 \approx n_s RT \frac{V_2}{V_2} \]

(25)

This is just van’t Hoff equation (see Fig[11] and Eq[11] for osmotic pressure.

If a standard atmospheric pressure is an initial pressure \( p = P_0 \) the compartment with solvent is under negative pressure for a molar concentration of solute \( n_s / V_1 \approx 10^{-3} \).

\[ \frac{n_a}{V_1} \approx 0.03 \text{mol/l}. \]

(26)

where \( n_a/V_1 \) is molar concentration of the air at sea level. It is about 0.03mol/l. On the other hand the molar concentration of water is approximately 50mol/l. This means that solvent is under negative pressure already for small relative concentration of solute \( n_s/n_{solvent} \approx 10^{-3} \).

IV. WATER UPTAKE IN TALL TREES

There are two transport systems of the fluids in trees. Water with some minerals and enzymes (sap) flow upward through the system of non-living cells called xylem. A solution rich with photosynthetic sugar (sucrose) flows through another system of living cell called phloem \[14\]. There is still no consensus about the mechanism of the sap ascent through xylem.

In Münch \[15\] model xylem and phloem are coupled via semipermeable membrane. Assuming that the total volume of the xylem and phloem is constant the sap in xylem, according to foregoing analysis, is under negative pressure. The reported molar concentrations of the sucrose \[16\] in phloem are 0.2 – 0.7mol/l. This concentration is enough large to cause the negative pressure in xylem that can pull the sap to the top of tall trees. We will not discuss this problem here in details since it will be the subject of separate paper.
V. CONCLUDING REMARKS

The standard textbooks on thermodynamics [1, 2, 3] introduce a pressure, within kinetic theory of gases, to describe the state of the free gas. Due to the weakness of cohesive forces in gases these systems can not be under tension. This property of the gases served as the basis for an extrapolation of the pressure as the positive definite value to other systems. However the extension of the concept of pressure to the liquids under tension leads to the notion of the negative pressure as well defined physical quantity.

We show in this paper that solvent in osmotic process under a constant volume can be in the state of negative pressure. Generally the state of negative pressure in pure liquids is metastable one. The question arises does this property holds for a solvent in osmosis under constant volume. This question will be the subject of our next work.

We have suggested here that the osmosis under constant volume can be responsible for the sap ascent in tall trees. The problem of the suction force in trees is still open question and we will devote a separate paper to this issue, too.

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