

# A Numerical Study of Molecular Motion in the Osmotic Equilibrium

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With the aid of molecular dynamics, osmotic equilibrium between ideal solution and pure solvent separated by semi-permeable membranes is investigated numerically. The method using phantom molecules is developed to model the membranes reflecting solute molecules. The validity of van't Hoff law for the osmotic pressure is confirmed over a range of concentration up to 0.1 in mole fraction.

## 1 INTRODUCTION

The osmosis is a fundamental subject encountered in many fields of study, including biology, chemistry and medicine, as well as physics. As is well known, some of biological and artificial membranes are permeable less to dissolved solutes, but more to water. Suppose that, by such a semi-permeable membrane, a dilute solution and a more concentrated solution are separated adjacently from each other under an external pressure. A solvent movement across the membrane from the dilute side to the other side, the so-called osmotic flow, will be driven spontaneously. The osmotic flow is prevented by a difference between external pressures on the solutions, which is termed osmotic pressure. A static state achieved finally subject to the osmotic pressure is "osmotic equilibrium". The physiological saline used to maintain living tissue is normally designed to be isotonic to body fluids, otherwise the osmotic pressure acting on membranes results in the rupture of blood vessels and tissues.

The formulation of osmotic equilibrium was first established by J. van't Hoff<sup>1)</sup> in 1887. Since the establishment, a variety of studies have been worked out to determine the magnitude of the osmotic pressure. According to the classical thermodynamics, the osmotic pressure for a dilute solutions is calculated by taking into account chemical potential  $\mu$ . Suppose that a solution consisted of  $n_0$  solvent molecules and  $n_1$  solute molecules is in contact with pure solvent across a semi-permeable membrane. In terms of the mole fraction of solute  $x = \frac{n_1}{n_0+n_1}$ , the chemical potential for solvent in the solution side is  $\mu_0(\theta, P) - k_B\theta \ln \frac{1}{1-x}$ , where  $\mu_0$  is the chemical potential for the pure solvent at temperature  $\theta$  and external pressure  $P$ . Since solvent molecules move freely across the membrane, the chemical potential should be identical in both the solution side and the pure solvent sides. If temperature is identical in both sides, the difference of external pressure between these sides is

necessary in the equilibrium, and thus

$$\left(\frac{\partial\mu_0}{\partial P}\right)_T \Delta P \approx x k_B \theta \quad (1)$$

is satisfied.

Compared to the thermodynamical procedure, the description for osmotic equilibrium based on a kinetic molecular theory remains however still rather incomplete<sup>2)</sup>, to our knowledge. It may be of interest to see that considerations of the molecular motions based on the classical dynamics will lead to the same results obtained by van't Hoff, and also for the reason that this point of view provides a more vivid picture of molecular motions at the equilibrium. Thus, in the present study, we first employ the molecular dynamics simulation for Lennard-Jones molecules to reproduce a real liquid numerically. Introducing solutions of the liquid to the reservoir separated into a couple of regions by semi-permeable membranes, we realize an ideal of osmotic equilibrium. The validity of van't Hoff law for the osmotic equilibrium is examined.

## 2 FORMULATION AND NUMERICAL METHOD

We employ the molecular dynamics to investigate a conventional micro-canonical ensemble of  $N$  mono-atomic molecules, enclosed in a reservoir with a volume  $V = L_x L_y L_z$ . The molecules interact through a two-body potential of the Lennard-Jones type,

$$\phi(r) = 4\varepsilon \left\{ \left(\frac{r}{\sigma}\right)^{-12} - \left(\frac{r}{\sigma}\right)^{-6} \right\},$$

with the cutoff radius  $r_{\text{cut}} = 2.5\sigma$ . The problem is to integrate the equation of motion according to the classical mechanics,

$$m \frac{d^2 \mathbf{x}_i}{dt^2} = \sum_{j(\neq i)} \mathbf{f}(\mathbf{x}_j - \mathbf{x}_i),$$

where  $\mathbf{x}_i$  is the position of the  $i$ -th molecule at time  $t$  and  $\mathbf{f}(\mathbf{r}) = -\frac{\partial\phi}{\partial\mathbf{r}} \frac{\mathbf{r}}{r}$ . As the time-development numerical scheme, we adopt the velocity Verlet method with  $\Delta t = 5 \times 10^{-3}$  with the aid of the neighbour list method<sup>3)</sup>.

Below, all the quantities will be measured in the following reduced units: The lengths are specified in units of  $\sigma$ , the temperatures in units of  $\varepsilon/k_B$ , and masses in units of  $m$ . For argon, these values are 3.405Å, 119°K and 39.95g/mol, and therefore the time unit is  $\sqrt{\sigma^2 m / \varepsilon} = 2.156\text{ps}$ . Throughout the present study, the density of the molecules  $\rho$  is kept to be 0.807, which is adjusted to be comparable with that of liquid argon. The thermodynamical quantities presented are basically the long-time average, which is denoted by  $\langle \cdot \rangle = \frac{1}{T} \int_0^T dt \langle \cdot \rangle$  unless noted otherwise.

## 3 RESULTS AND DISCUSSION

### 3.1 Liquid in a cubic reservoir

First, we will estimate the pressure of an assembly of real argon atoms equivalent to our system and then show the assembly is in the liquid phase. The pressure  $p_{\text{sr}}$  can be calculated by applying Clausius' virial theorem to our Lennard-Jones system:  $p_{\text{sr}} = \frac{N}{V} k_B \theta + \frac{1}{6V} \sum_{i \neq j} \langle (\mathbf{x}_i - \mathbf{x}_j) \cdot \mathbf{f}(\mathbf{x}_j - \mathbf{x}_i) \rangle$ , where  $k_B$  is Boltzmann constant,  $V = L_x L_y L_z$  is the volume of the reservoir, and  $\theta$  is the temperature. Following Verlet<sup>3)</sup>, the contribution to the second term in the right hand by the molecules at a distance over the cutoff length can be moreover approximated with the aid of the radial distribution function  $g(r)$ , and finally we obtain

$$p_{\text{sr}} \approx \frac{N}{V} k_B \theta + \frac{1}{6V} \sum_{\substack{j \neq i \\ |\mathbf{x}_i - \mathbf{x}_j| \leq r_{\text{cut}}}} \langle (\mathbf{x}_i - \mathbf{x}_j) \cdot \mathbf{f}(\mathbf{x}_j - \mathbf{x}_i) \rangle + \frac{N^2}{6V^2} \int_{r_{\text{cut}}}^{\infty} \int_0^{\pi} \int_{-\pi}^{\pi} g(r) r \mathbf{f}(\mathbf{r}) \cdot d\mathbf{r}.$$

Table 1: Parameters and thermodynamical quantities in preliminary studies carried out to prepare an equilibrium state of the liquid. Total number of molecules  $N$ , total simulation time  $T$ , volume  $V$ , density  $\rho$ , temperature  $\theta$ , and pressure  $p + p'$ .

	non-dimensional	dimensional
$N$	2048	
$T$	$5 \times 10^4$	$0.108[\mu\text{s}]$
$V$	$2.54 \times 10^3$	$99.7[\text{nm}^3]$
$L_x \times L_y \times L_z$	$34.4 \times 8.59 \times 8.59$	$11.7[\text{nm}] \times 2.90[\text{nm}] \times 2.90[\text{nm}]h$
$\rho$	0.807	$1.36 \times 10^3[\text{kg}/\text{m}^3]$ <small>(<math>29.3[\text{cm}^3/\text{mol}]</math>)</small>
$\theta$	0.837	$100[\text{K}]$ <small>(<math>-173[^\circ\text{C}]</math>)</small>
$p$	0.97	$4.07 \times 10^5[\text{hPa}]$
$p'$	-0.70	$-2.93 \times 10^5[\text{hPa}]$

Henceforth, we abbreviate the sum of the first and second terms in the right hand side just as  $p$  and the rest as  $p'$ . At preliminary studies carried out to prepare an equilibrium state of the liquid in a reservoir with periodic boundary conditions,  $p$  is 0.97, while  $p'$  is  $-0.70$  by approximating  $g(r) = 1$  for  $r > r_{\text{cut}}$  (see Fig. 1). Therefore  $p_{\text{ar}}$  is 0.27. The corresponding point plotted in a phase diagram for argon (Fig. 3) is apparently inside the liquid phase. This pressure value is small compared to the values calculated based on the equation of state for the Lennard-Jones molecular fluid presented by Johnson et al<sup>4)</sup> ( $p_{\text{ar}} = 0.303$ ) and recently by Boltachev et al<sup>5)</sup> ( $p_{\text{ar}} = 0.317$ ). The difference could be explained mainly by the used approximation to  $g(r)$ , but partly by that both  $N$  and  $r_{\text{cut}}$  are smaller than those used in the current standard researches. Additionally, it is confirmed that the assembly is in the liquid state in the  $\theta$ - $\rho$  projection of phase diagram for Lennard-Jones molecular fluid<sup>6)</sup>.

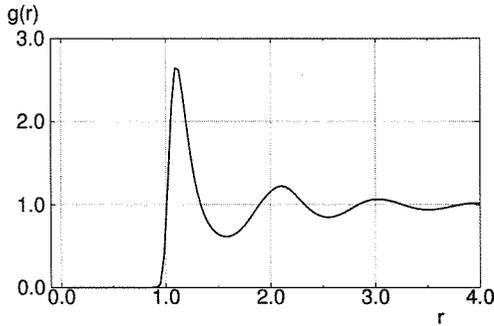


Fig. 1: Radial distribution function  $g(r)$  in  $pc2$ .

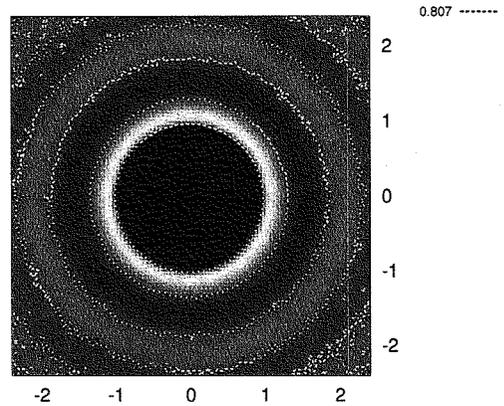


Fig. 2: The pair density function at  $x - y$  cross section ( $z = 0$ ).

Unfortunately in the present study, the number of molecules and the size of the system is not satisfactory compared to the recent standard research, while the original focus in the present study is to establish a simple system of an ideal solution to model the osmotic equilibrium, but not to realize a liquid with the precisely-measurable thermodynamical properties. One would however think that the restriction of the size causes an anisotropy or some singular structural

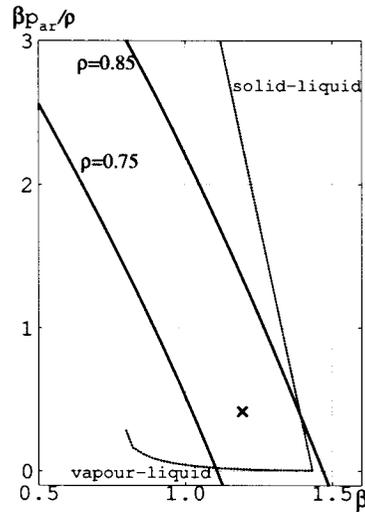


Fig. 3: The compressibility factor  $\beta p_{ar}/\rho$  as a function of  $\beta = 1/k_B\theta$ . Curves correspond to isochores  $\rho = 0.85, 0.75$  from MD calculation by Verlet<sup>3)</sup>. The preliminary studies corresponds to a cross. The dashed curves correspond to the vapour-liquid and solid-liquid coexistence states which are an experimental result compiled by Din<sup>7)</sup>.

properties in the system, which would cancel the assumption on using the radial distribution function in the virial theorem. The anisotropy would be caused also by that the aspect ratio of the reservoir differs from an unit. Here, we calculated the 3-dimensional pair density function,  $\rho(\mathbf{x})dV = \langle \sum_{i,j=0}^N \delta((\mathbf{x}_j - \mathbf{x}_i) - \mathbf{x}) \rangle$ . If the system is isotropic as well as homogeneous, the pair density function is a function only of the separation  $|\mathbf{x}|$ ; therefore the radial distribution function obtained is possible to apply in the virial theorem. As an example, we present Fig. 2, the  $x$ - $y$  cross section ( $z = 0$ ) of  $g(x, y, z)$ , where would appear to guarantee that the anisotropy is relatively small.

### 3.2 Solutions separated by a semipermeable membrane

Next, let us discuss the osmotic equilibrium. An equilibrium state of ideal solution in contact

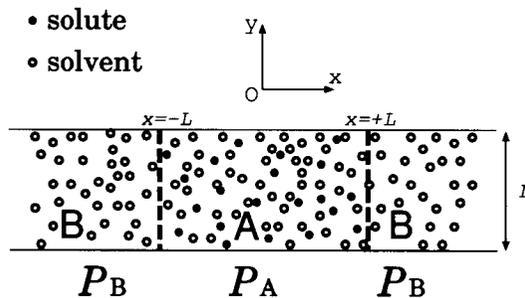


Fig. 4: The schematic view of the  $xy$  projection of the reservoir filled with solution in A and pure solvent in B contacted by a semi-permeable membrane (thick-dashed line).  $n_0$  solvent molecules are described by  $\circ$ , while  $n_1$  solute molecules are done by  $\bullet$ . The membranes prevent the solute molecules from leaking out of A, then the liquids in A and B are the solution and the pure solvent, respectively.

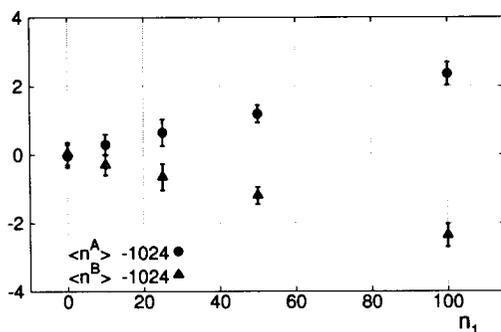


Fig. 5: The dependence of the mean number of molecules in the region A and B to the solute concentration  $c_1 = n_1/V_A$ .

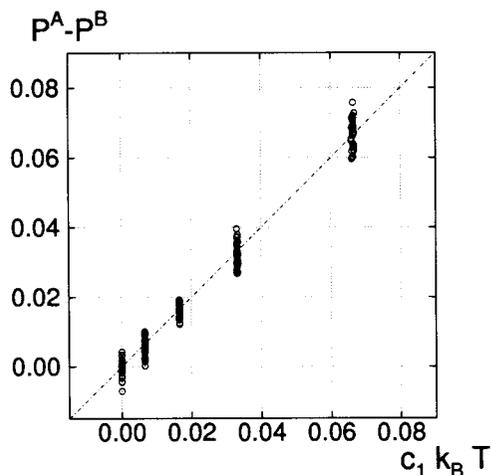


Fig. 6: The dependence of the osmotic pressure  $P_A - P_B$  to the solute concentration  $c_1 = n_1/V_A$ . The line with a slope of a unit corresponds to van't Hoff law.

with pure solvent across semi-permeable membranes is numerically realized in the reservoir introduced in the preliminary studies. As described in Fig.4, we suppose a couple of semi-permeable membranes dividing the space of the reservoir into the regions A and B with equal volume. The region A is between the membranes located at  $x = \pm L$ , where  $L$  is set to 8.59. The system consists of  $N = 2048$  Lennard-Jones molecules,  $n_1$  of which are solute molecules and all the rest ( $n_0 = N - n_1$ ) are solvent ones. Here, the suffices  $i = 0, 1$  refer to the molecule species, solvent and solute, respectively. The initial state is obtained by choosing random  $n_1$  solvent molecules in the region A as solute ones at an equilibrium state attained by the aforementioned simulation performed with neither solute nor membrane. The only difference between solute and solvent molecules in the time development is just the affection to their motions by the membranes. We append an extra term to the equation of motion for the solute molecules so that the membranes reflect all the solute molecules. The extra term is the force by a phantom molecule which is an image of the considered solute molecule in mirrors located at the membranes. For instance, for the  $i$ -th molecule chosen as a solute molecule the extra term is  $\mathbf{f}(\mathbf{X}(\mathbf{x}_i) - \mathbf{x}_i)$ , where the position of the phantom molecule for a solute molecule located at  $\mathbf{x}_i$  is denoted as  $\mathbf{X}(\mathbf{x}_i)$ , which is  $(L - x_i, y_i, z_i)$  in the orthogonal coordinate. The interaction between the phantom molecule and the solute molecule is as same as that between the others. As a result, all the solute molecules are confined even in the region A. The membranes never affect the motion of any solvent molecule. Solvent molecules are all able to move freely as far as in the reservoir. Thus, for  $n_1 > 0$ , the region A is filled with an solution, while the region B is done with a pure solvent. It should be noted that the solution can be considered as an ideal solution, because the forces of interaction between solvent and solute molecules are identical to those acting between the solvent molecules themselves. We carried out the simulations for  $n_1 = 10, 25, 50$  and 100. If we suppose the mean number of molecules in the region A as  $N/2$  for ease, the range of the concentration of the solution considered here corresponds to  $0.01 \sim 0.1$  in mole fraction.

Here, we denote the number of the molecules in the region A and B at time  $t$  as  $n^A(t)$  and  $n^B(t)$ , respectively. One could be concerned in the long-time average of the excess of  $n^X$  ( $X=A,B$ ) over  $N/2 = 1024$ , which is referred to as  $\langle \Delta n^X \rangle$  below. Fig. 5 shows the dependence of  $\langle \Delta n^A \rangle$

on  $n_1$ . In case of the system with no solute,  $\langle \Delta n^A \rangle = \langle \Delta n^B \rangle = 0$  owing to the symmetry of the system. With the increase of  $n_1$ ,  $\langle n^A \rangle$  increases (and  $\langle n^B \rangle$  decreases) linearly but with a slope further smaller than an unit as shown in the figure. Note that if the interaction among molecules could be negligible as in the ideal gas,  $\langle \Delta n^A \rangle = n_1/2$  would be satisfied exactly.

Taking into account that an equilibrium state attained with no solute is adopted as the initial distribution for these simulations, we may consider  $\langle \Delta n^A \rangle$  as the net number of the solvent molecules that moved dynamically across the membrane due to osmosis after the initial equilibrium state. Thus, the increase of  $\langle \Delta n^A \rangle$  with  $n_1$  means that dissolving solutes in the solution results in the solvent movement across the membrane from the dilute side to the more concentrated side, what we call, osmotic flow.

Finally, let us discuss the osmotic pressure in the system. Applying the virial theorem to the solutions, we will here examine the pressure in each region,  $P^A$  and  $P^B$ . One would think the correction to pressure by the radial distribution function is only applicable to the bulk fluid not but to systems with surfaces. In the present system, the planes,  $x = \pm L$ , are considered as a kind of surface for solute molecules, so the thermodynamical properties of the system should be corrected appropriately. However, we expect that the osmotic pressure, what we are here interested in, is affected little by the correction. Firstly, all the molecules in the system are Lennard-Jones molecules with the same parameters. Moreover, because the osmotic pressure is not pressure itself but the difference of pressures as mentioned below, the correction seems to be small enough, even if it exists. Originally the osmotic pressure is defined as the excess pressure of the concentrate side to the dilute side that is necessary to prevent solvent movement across the membrane, the osmotic pressure in the system is equal to  $P^A - P^B$ . In Fig. 6, the osmotic pressure is represented by circles for solute concentration  $c_1 = n_1/V_A$ . The osmotic pressure is not deviated clearly from the van't Hoff law in the range of the concentrations considered in the present study.

Fig. 7 shows the mean number density of solute and solvent molecules in the  $x$  direction in case of  $n_1 = 100$ , where the width of bins is set to be  $L_x/32$ . If the interaction between different type of molecules would be negligible, the number density of solute molecules  $c_1$  would be 0.0767 uniformly in the region A, and that of solvent molecules  $c_0$  0.788 uniformly all over the reservoir. In practice, the number density of solvent molecules is however not uniform over all the reservoir. Solute molecules are prevented from leaking out of the region A mainly due to the repulsive force by phantom molecules. Due to the interaction with the solute molecules, solvent molecules are removed from the region A, so the number density of solvent molecules is reduced almost uniformly in the region A, and increased in the region B. On the other hand, as seen in the figure, the number density of all the molecules  $c_{0+1}$  in the region A is somehow almost the same as that in the region B. Although less detail is given here, based on the present result, we performed the simulation of L-J molecular fluids ( $N = 8192, n_1 \leq 400$ ) in the reservoir with the reflection condition. It is also observed that the osmotic pressure examined in the reservoir is subject to the van't Hoff law, which will be elaborated and discussed elsewhere.

## 4 SUMMARY

In summary, osmotic equilibrium between ideal solution and pure solvent separated by semi-permeable membranes has been investigated using molecular dynamics. The method using phantom molecules was developed to model the membranes reflecting solute molecules. It was confirmed that van't Hoff law is valid in a range of solute concentration.

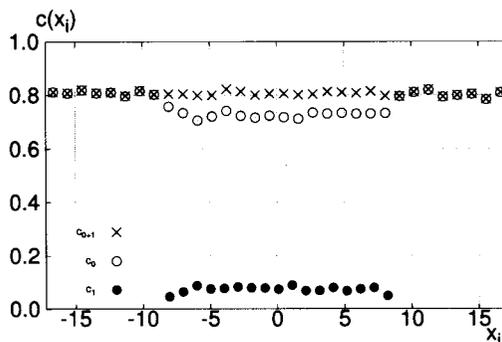


Fig. 7: The mean number densities of solute molecules (●), solvent molecules (○), and the sum of them (×), in case of  $n_1 = 100$ .

## 5 ACKNOWLEDGEMENTS

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