MANIFESTATION OF ENERGY AND ENTROPY OF PARTICLES IN A BOX

A PREPRINT

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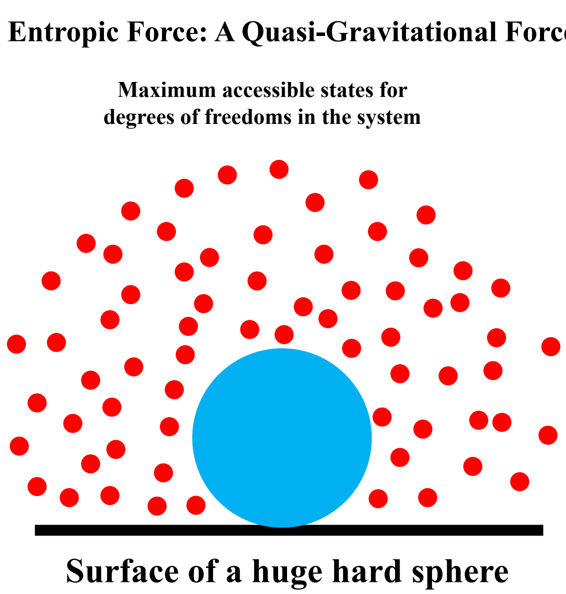
January 7, 2022

ABSTRACT

The energy and entropy, expressed in free energy, determine the behavior of a system. Therefore, infinite knowledge of these two quantities leads to precise prediction of the system's trajectories. Here, we study how the energy and entropy affect the distribution of a two-component system in a box. First, using a model, we intuitively show that large particles prefer to position at contact with the wall as it accompanies an increase of the system's entropy. We intuitively show that this is a consequence of maximizing the accessible states for fluctuating degrees of freedom as a portion of excluded volumes reside outside of the box when they locate near the wall. Then we employ molecular dynamics simulations to extract the effect of entropy and energy on the binary mixture distribution and how they compete with each other to determine the system's configuration. While particle-particle and particle-wall attraction energies affect the distribution of particles, we show that the emergent entropic forces — quasi-gravitational — have a significant contribution to the configuration of the system. This system is realized clearly for a binary mixture of hard spheres in a box with reflective walls.



Keywords Entropy · Energy · Hard spheres · Force

1 Introduction

The contribution of entropy to the configuration of a system is nontrivial. If we have all the information about the interaction energies of a system, we only can make a precise prediction of a system's behavior when we fully understand the entropy of that system. The energy and entropy which formulate the free energy determine how a system behaves at a certain temperature (1; 2).

To understand the energy and entropy contributions to the behavior of a system, we study their effects on the distribution of a binary mixture of particles in a cubic box. Studying a binary mixture as a two-component system allows us to understand the relative effect of volume and energy-related parameters of particles on the phase behavior of a confined system. A confined system carries characteristics distinguishable from those of a bulk system owing to energy and entropy effect of walls on the configuration of the confined system (3; 4; 5; 6). It is intuitively comprehendible that energy affects the configuration of particles in a box. Strong particle-particle attraction energies lead to nucleation and growth of particles to form clusters inside the box and strong wall-particle attraction energies lead to the accumulation of particles adjacent to the wall. On the other hand, the effect of entropy as a counter-intuitive property can be manifested clearly when the energy effect is eliminated from the system. A satisfying representative of such a system is a hard-sphere model in a box with hard potential walls (reflective walls).

Hard spheres cannot overlap owing to infinite repulsive energies between particles at contact. The volume that a hard-sphere excludes other hard spheres to occupy is identical to a sphere at the center of a hard-sphere with a diameter equal to the center-to-center distance of two contacting hard spheres. This distance is the sum of the radii of two hard spheres at contact (7). The phase space that a particle forbids the other counterpart particle to occupy is called excluded volume and schematically demonstrated in Fig. 1.

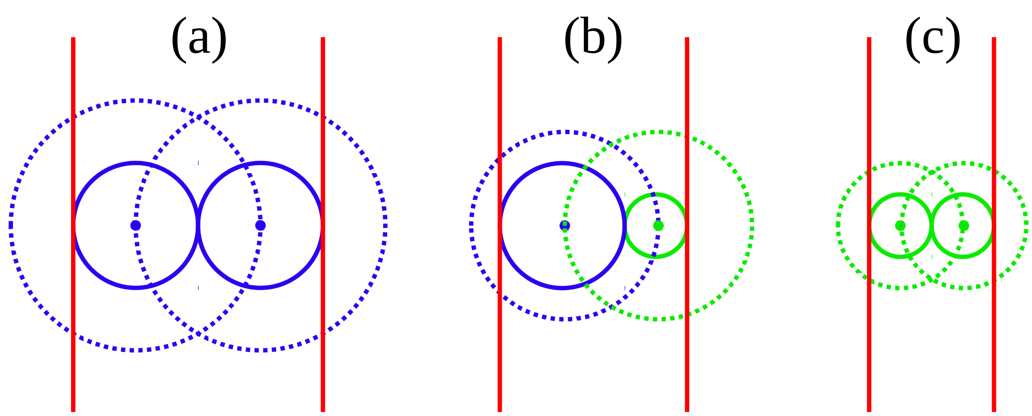


Figure 1: A 2D representation of excluded volume when two large discs (a), one large and one small disk (b), and two large discs (c), are at contact with each other and sandwiched with two vertical walls. The walls are represented with red lines. The large and small discs are represented with blue and green circles, and blue and red dashed circles represent corresponding excluded volumes.

When hard spheres are positioned next to the wall of a box, a portion of the excluded volume lays outside of the box and leaves more residual space for the rest of the hard spheres. This is entropically favorable as the entropy of a system increases with the increase of accessible microscopic states in phase space for degrees of freedom. As a result, hard spheres statistically prefer to locate in the regions adjacent to the wall. Accordingly, in a binary mixture of hard spheres with two different radii, the larger spheres, relatively, prefer to occupy the regions next to the wall (8; 9; 10). This entropic force that attracts hard spheres to the wall and is arisen from the depletion zone is called depletion force.

Similarly, the depletion force creates attraction between large hard spheres in presence of small hard spheres or so-called depletants (11; 12; 13). A similar phenomenon is observable for real particles containing interaction energies, however, the energy effect interferes with entropic forces, and realization of the entropy effect can be ambiguous.

To understand the depletion phenomenon and entropy effect on the distribution of particles in a two-component system, first, we use a theoretical model to study two extreme cases. We assume either all the large or small spheres lay adjacent to the wall, and for each case, we calculate excess entropy of the system — the difference between the entropy of the real and ideal system under the same temperature and pressure. Then we employ the molecular dynamics method to investigate the effect of energy and entropy and their competition on the distribution of particles in the dynamical systems with different interacting potentials. To do this, we studied different variations from systems with Lennard-Jones potential for walls and particles to systems with reflective walls and hard spheres.

2 Methods

We explain the calculation of excess entropy from the Carnahan-Starling equation of state. Then we explain the method used for molecular dynamics calculations.

2.1 Excess entropy

To calculate entropy, Helmholtz free energy is used as follows:

$$dA = -sdT - pdV \tag{1}$$

Helmholtz free energy equation of state is a state function that only depends on the state of the system regardless of the path that is taken to reach that state. Therefore, the following Maxwell equation from the Helmholtz free energy equation is extracted using Euler relation for the exact differential equation:

$$(\frac{ds}{dV})_T = (\frac{dp}{dT})_V \tag{2}$$

Entropy difference is derived by integration over Maxwell relation:

$$\int_{s_1}^{s_2} ds = \int_{V_1}^{V_2} (\frac{dp}{dT})_V \, dV \tag{3}$$

As $\rho = \frac{N}{V}$, we rewrite Eq. 3 as equation Eq. 4:

$$\int_{s_1}^{s_2} ds = -\int_{\rho_1}^{\rho_2} (\frac{dp}{dT})_V \, \frac{d\rho}{d\rho^2} \tag{4}$$

To derive excess entropy, we substitute s_2 with ideal entropy (s_{id}) and s_1 with real entropy (s). Therefore:

$$\begin{array}{lllll} s_1 = s_{id} & \longrightarrow & V_1 = \infty & \longrightarrow & \rho_1 = 0 \\ s_2 = s_2 & \longrightarrow & V_2 = V & \longrightarrow & \rho_2 = \rho \end{array} \tag{5}$$

Here, we use the Carnahan-Starling equation of state for hard spheres: (14)

$$Z = \frac{1 + \eta + \eta^2 - \eta^3}{1 - \eta^3} \tag{6}$$

where $Z = pV/NkT$ is the compressibility factor, and $\eta = \rho\pi\sigma^3/6$ is the packing fraction for hard spheres. In this regard, the following equation is extracted as follows:

$$Z = \frac{NkT}{V}(\frac{1 + \eta + \eta^2 - \eta^3}{1 - \eta^3}) \tag{7}$$

Implementing Eqs. 6 and 7 into Eq. 4 and knowing that $s_{ex} = 0$ for ideal gas where $\rho = 0$, and therefore, $\eta = 0$ (Eq. 5), the Eq. 8 is extracted as follows:

$$\frac{s_{ex}}{Nk} = 3 - \frac{2}{1-\eta} - \frac{1}{(1-\eta)^2} \tag{8}$$

In Eq. 8, s_{ex} is the excess entropy that we used in our calculations.

2.2 Molecular Dynamics Calculation

We performed MD simulations using the LAMMPS package. We created a data file for the positions of particles in a box. The fixed wall was used to create a box. We used either Lennard-Jones (Eq. 9) or hard-sphere potentials (Eq. 10).

$$V = 4\epsilon[(\frac{\sigma}{r^{12}}) - (\frac{\sigma}{r^{6}})] \tag{9}$$

To create a hard potential for particles in LAMMPS, the following homographic function was used shown in Eq. 10:

$$V = \frac{\sigma}{r^{12}} \tag{10}$$

This function represents the repulsion part of Lennard-Jones potential. The homographic function with high power of r generates great repulsive force between particles as the distance between them becomes close to zero such that they never occupy each other's volume. Also, they barely feel each other when particles are not at a close distance from each other. Therefore, this homographic function is a proper representative of hard-sphere potential.

We used an NVT ensemble where the temperature was set to 300 K using the Nose-Hoover thermostat. Verlet algorithm was applied for Integration over Newtonian's law of motion with a timestep of 1fs. We used a total of 8000 particles of two different sizes in a box with dimensions of 100 angstroms. The frames of trajectories were stored every 1ps for analysis.

3 Results

Imagine two two-dimensional (2D) boxes containing two hard discs. In each, two hard disks differ in diameter (Fig. 2). Assume, in one box, the larger particle is fixated adjacent to the wall, and the smaller particle is distributed in the residual space — in discretely partitioned squares with the dimensions equal to the diameter of the small particle (Fig. 2a). Now, imagine in the other box, the smaller particles are fixed adjacent to the wall, and the larger particle is distributed in the residual space of the box — in discretely partitioned squares with the dimension equal to the diameter of the larger particle (Fig. 2b).

From Fig. 2a and 2b, it can be intuitively deduced that the accessible states for the smaller particle are significantly more than ones for the larger particle, and consequently, it possesses larger configurational entropy. Even though the residual space for the large particle in Fig. 2a is larger than Fig. 2b for smaller particle, the number of squares for the small particle in Fig. 2b is significantly more than the larger particle in Fig. 2a. Therefore, the system in Fig. 2b has higher entropy than the system in Fig. 2a, consequently, the configuration presented in Fig. 2a is more favorable. This is called the entropy effect, and the quasi-gravitational force that attracts the larger particles to the surface of the wall is called the depletion force. Here, the question that comes to mind is: Is entropy larger when the larger disk is adjacent to the wall and the small disk is distributed in the residual space than when the larger disk is fixated in the middle of the box and the small disk is distributed in residual space? It is certainly higher when the larger disk is next to the wall as a portion of excluded volume locates outside of the box which leads to an increase in the number of accessible states for the smaller disk.

We understand that if we have more than one particle of each type with equal populations, the portion of the total excluded volume that locates outside of the box is larger when large particles are positioned adjacent to the wall. To quantitatively measure the entropy, we used excess entropy ($s_{ex} = s - s_{id}$) expression derived from Carnahan-Starling equation of state for hard spheres (described in Methods) (14). We developed a model containing a binary mixture of hard spheres in a three-dimensional (3D) box with dimensions of 100 Å. For the sake of simplicity, we assumed the excluded volume of particles does not overlap with each other. With this assumption, the occupied volume is calculated by the following equation:

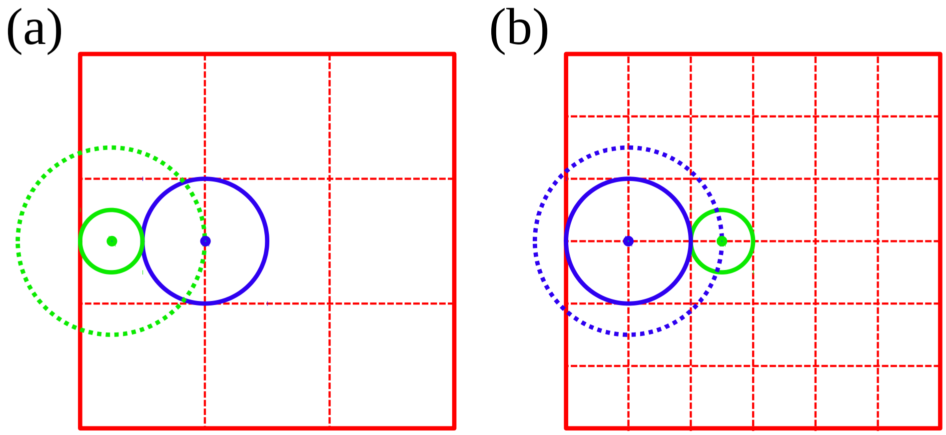


Figure 2: A schematic representation of a two-component system in a 2D box (red square) when a small disc (green circle) is next to the wall (a) and a large disc (blue circle) is next to the wall (b). The corresponding excluded volumes of small and large discs are represented with green and blue dashed circles. All the possible accessible microscopic states of the phase space for large disc (a) and small disc (b) are partitioned with red dashed lines in the system.

$$V_{occupied} = \frac{2}{3}\pi r_t^3 + \pi r_t^2 r_w - \frac{1}{3}\pi r_w^3 \tag{11}$$

where r_w is the radius of spheres adjacent to the wall, and r_m is the radius of the particles distributed in the residual space. r_t is sum of the radius of two spheres ($r_t = r_w + r_m$).

We studied four different scenarios as follows: (I) Large particles are fixated adjacent to the wall and small particles are distributed in residual volume. (II) Large particles are fixated in the middle of the box and small particles are distributed in residual volume. (III) Small particles are fixated adjacent to the wall and large particles are distributed in residual volume. (IV) Small particles are fixated in the middle of the box and large particles are distributed in residual volume. We calculated the excess entropy as a function of the number of particles and the size of large particles for each scenario (Fig. 3). The system's entropy for hard spheres is always smaller than the entropy for an ideal gas system as ideal gas does not occupy any space, and as a result, they can overlap. Therefore, the excess entropy $s_{ex} = s - s_{id}$ is always negative. Furthermore, excess entropy decreases with the increase in size and number of particles as the accessible volume for the distribution of particles decreases.

Our results show that the excess entropy is smaller when larger particles are fixated in their position and smaller particles distributed in residual space (Figs. 3a and 3b) than when smaller particles are fixated in their position and larger particles are distributed in residual space (Figs, 3c and 3d). Also, the excess entropy is smaller when larger particles are adjacent to the wall and small particles are distributed in residual space (Figs. 3a) than when the small particles are fixated adjacent to the wall and larger particles are distributed in residual space (Figs. 3c). Lastly, comparing Figs. 3a and 3c with corresponding Figs. 3b and 3d show that the excess entropy is lower when particles of one type are fixated adjacent to the wall and particles of the other type are distributed in residual space. Because a portion of the excluded volume of particles resides outside of the box and that frees more space for other particles to gain configurational entropy.

For further investigation on the distribution of particles in a cubic box, we performed molecular dynamics simulations as is described in Methods. To study the distribution of particles for each system in our simulations, we created a histogram of particles' positions across the x-axis of the 3D box over time using their trajectories after the system reaches an equilibrium state.

First, we simulate a system of Lennard-Jones particles in a box with Lennard-Jones walls (Supporting Information, Figs. S1 and S2). Fig. 4 shows that larger particles with large attractive forces toward each other relative to the walls

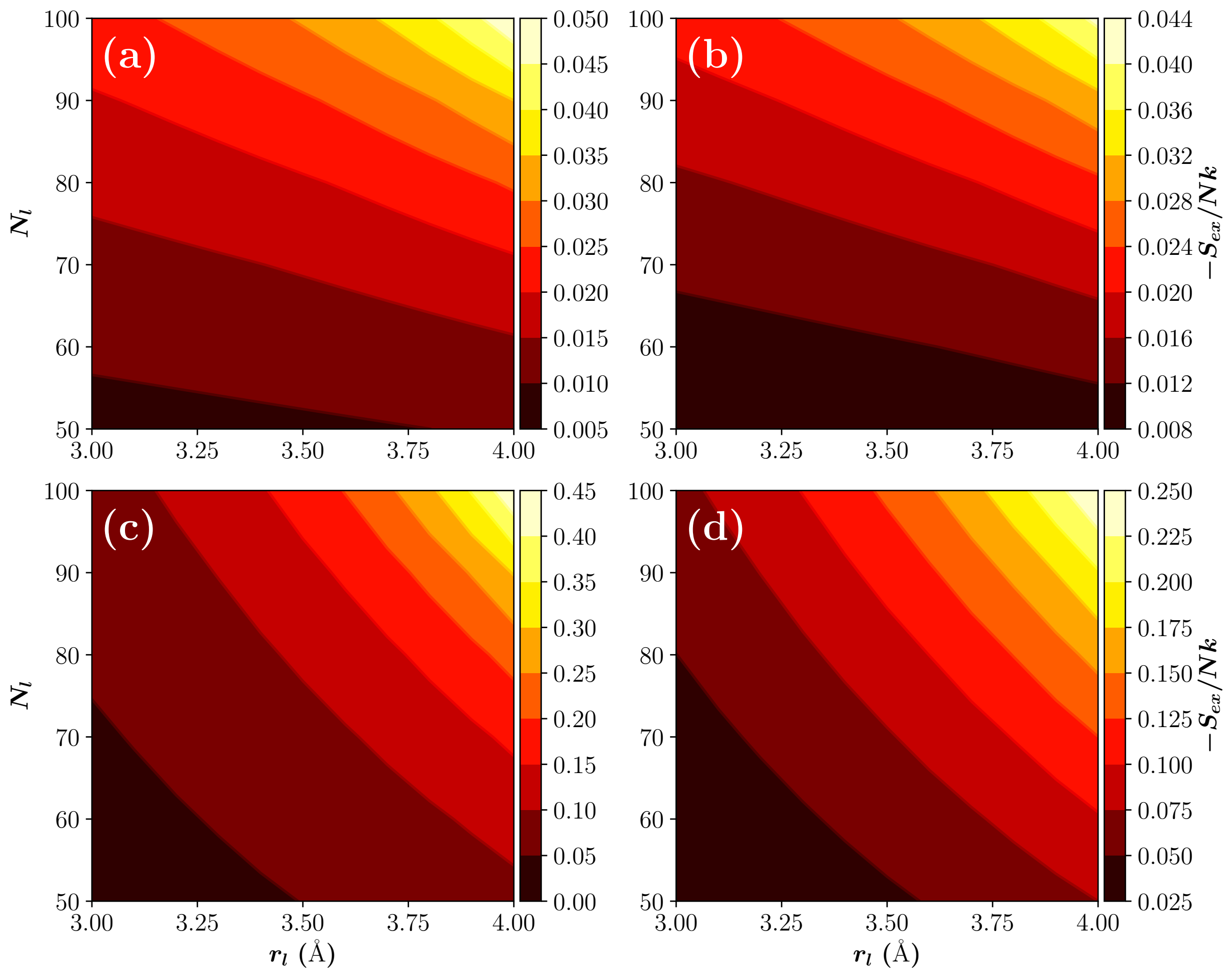


Figure 3: The calculated values of reduced excess entropy (s_{ex}/Nk) using Carnahan-Starling equation of state with respect to number (N_l) and radius (r_l) of large particles. Number of small particles (N_s) and N_l is equal, $N_s = N_l = N$.

form clusters — peaks in the distribution are indicative of the presence of clusters —, and small particles with small attractive forces toward each other relative to the walls are attracted to the walls.

It is intuitively expected that particles that outcompete the attractive forces from the wall eventually attract each other to form clusters. We observe that when large particle-particle attractive forces were set for larger particles, they form clusters inside the box within the 20 ns time frame of our simulations (Fig. 4 and Supporting Information, Figs. S1 and S2). Also when the volume of larger particles increases significantly while the energy-related parameters are the same for both types, the entropic and energic forces for accumulating the large particles next to the walls outcompete the energy and entropy for aggregation of clusters. Flat walls of the box can represent the surface of an enormous particle that strongly contributes to the entropy in attracting the larger particles in a binary mixture system (Fig. 4). We systematically changed the wall-particle and particle-particle attractive forces to dig more into the influence of energy on the distribution of particles inside the box. We understood that walls with lower wall-particle attractive forces relative to the particle-particle attractive forces lead to the distribution of particles in the box. In contrast, high wall-particle attractive forces relative to particle-particle attractive forces lead to the accumulation of particles next to the wall — entropic forces along with energic forces favor this event.

In the next set of simulations, we created a box with reflective walls using hard potentials and a binary mixture of Lennard-Jones particles. With this design, we eliminated the wall-particle attractive forces, and therefore, the energy effect from the walls on the distribution of particles. Now, both types of particles energetically tend to attract each other in the box, but entropically prefer to locate close to the wall. When particles are of the same size, the ones that have relatively high attractive forces form clusters, and the others with lower attractive forces, within the time frame of our

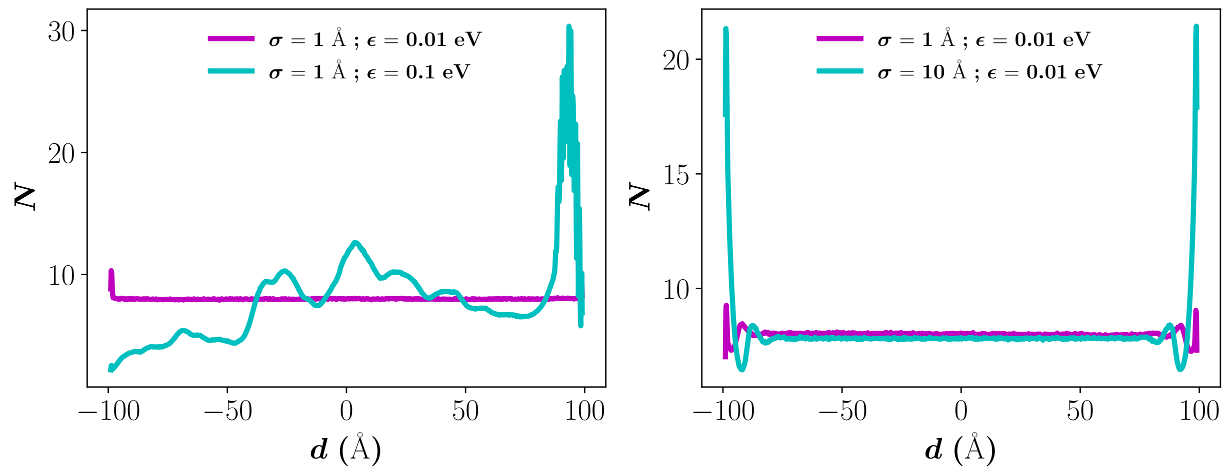


Figure 4: Distribution of a binary mixture of Lennard-Jones particles in a 3D box with Lennard-Jones walls — $\epsilon = 0.01$ eV. Both particles are of same mass — $m = 39.948$ gr/mol. Blue and purple lines show the population of large and small particles within a slab of 1 Å, respectively averaged over the ensemble measurements, across the x-axis of the box with a length of 200 Å.

simulation, distribute evenly in the box (Fig. 5 and Supporting Information, Fig. S3). To detect the entropy effect, we designed a binary mixture of particles with the same attractive forces, but significantly different in volume. We found that the population of larger particles in regions adjacent to the walls is substantial as this accompanies an increase of the entropy (Fig. 5 and Supporting Information, Fig. S4).

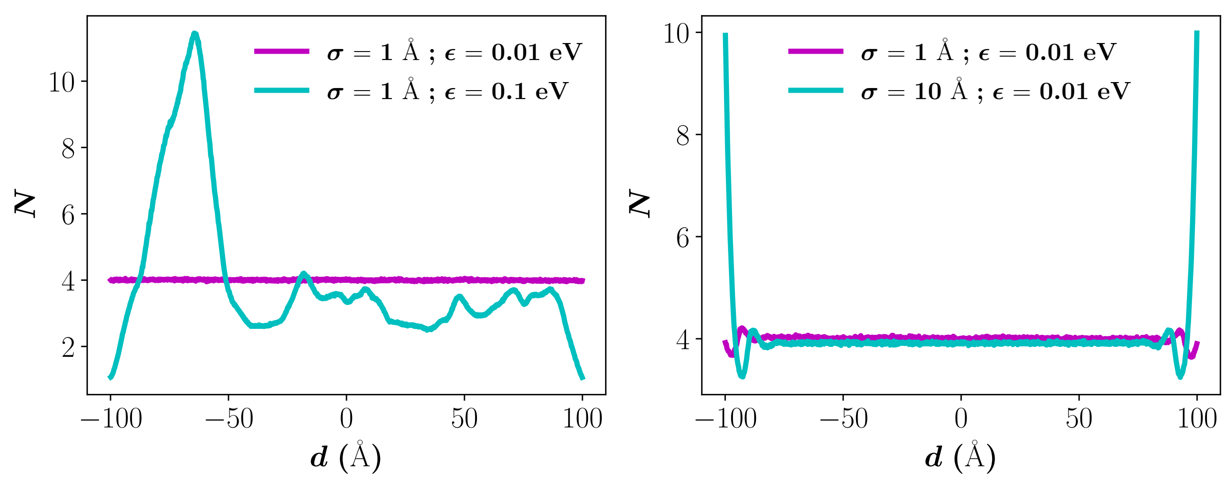


Figure 5: Distribution of a binary mixture of Lennard-Jones particles in a 3D box with reflective walls. Both particles are of same mass — $m = 39.948$ gr/mol. Blue and purple lines show the population of large and small particles within a slab of 1 Å, respectively averaged over the ensemble measurements, across the x-axis of the box with a length of 200 Å.

Fig. 5 implies that the entropic force that emerges from the depletion effect attracts particles toward the wall outcompete the energy effect that is the cause of particles aggregation in the box. We observe that the particles with low particle-particle attractive forces have a high tendency toward the wall owing to entropic forces. We found that, when we used single-type particles with high attractive forces, the energy effect outcompetes the entropy effect in the formation of clusters. On the other hand, particles with low attractive forces, in a one-component system, preferably accumulate adjacent to the wall. These results indicate that the entropy effect outcompetes the energy effect in favoring particles to a position adjacent to the wall in a weakly associating system. The simulations with hard spheres and Lennard-Jones wall also led to an accumulation of particles especially larger ones next to the wall (Supporting Information, Figs. S5 and S6)

To further clarify the entropy effect on the distribution of particles, we eliminated the particle-particle attractive forces, in addition to the particle-wall interaction that was imposed in the previous step, by designing a binary mixture of hard spheres in a box with reflective walls. As described in Methods, for hard spheres, we used a strongly repulsive potential for spheres at contact and approximately zero potential when they are not in contact. In this system, the energy effect that is responsible for the aggregation of particles, owing to particle-particle attractive forces, and accumulation of particles adjacent to the wall, owing to wall-particle attractive forces, are eliminated from the system. In this set of simulations, we systematically increased the radius of larger particles to further understand the relationship between the entropic force and the volume of particles. Fig. 6 and Supporting Information, Figs. S7 confirm the higher tendency of larger particles in laying next to the wall for hard-sphere with approximately zero attractive forces between particles.

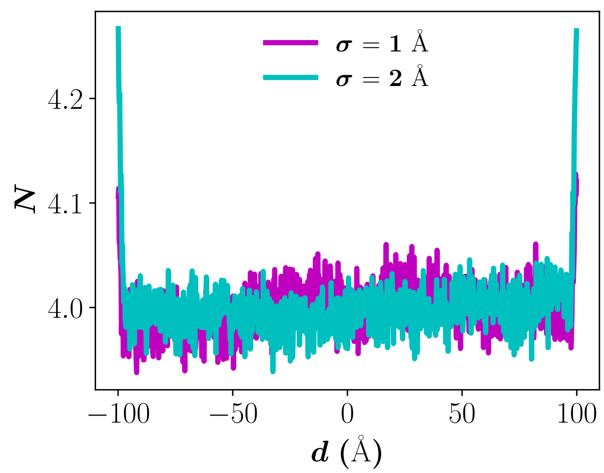


Figure 6: Distribution of a binary mixture of hard spheres in a 3D box with reflective walls. Both particles are of same mass — m = 39.948 gr/mol. Blue and purple lines show the population of large and small particles within a slab of 1 Å, respectively averaged over the ensemble measurements, across the x-axis of the box with a length of 200 Å.

Fig. 6 indicates that the entropy effect owing to depletion force attract larger particles to the wall — as if there is gravity that pulling particles toward the wall — as it creates larger residual space for smaller particles to gain a higher configurational entropy through the exclusion of excluded volume.

4 Discussion

Energy and entropy, two quantities that can define the character of a system are formulated into free energy in thermodynamics. Energy is a tangible concept as it is measurable that particles of a system attract and repel each other owing to their so-called fundamental forces between subatomic particles such as electrons and protons. Knowledge of the interaction energies between the constituents of a system is insufficient to fully predict the behavior of a system, and one must know the entropy to have a precise prediction. In contrast to energy, it is intuitively difficult to understand entropy. The constituents of a system, particles, bear random Brownian motions in a given temperature — temperature is a measure of the kinetic energy of particles which is exerted on particles of the system by collision with particles of a heat reservoir and other possible surrounding factors. A single particle with no energy at absolute zero Kelvin remains motionless in a phase space until a collision moves it to a particular direction in a stochastic manner. Each particle has infinite accessible microscopic states to possess in a continuum space with time's arrow. Here, we define each particle that can select a microscopic state for every individual displacement of kT — one bit of information — after a collision, one degree of freedom (15; 16). Therefore, in a system with n particles, the total of n degrees of freedom are available for random displacements at the microscopic level of that system (17). These collective random motions of particles in a system at a given temperature have two manifestations from two perspectives. While we studied one of these manifestations, we find it important to explain briefly both of them to emphasize the contribution of entropy in the behavior of a system. In this regard, first, we discuss the effect of a mechanical external force on a system with certain initial entropy at an initial temperature. Then we discuss the interior configuration of a system influenced by the entropy of that system at a given temperature.

Imagine an external field, even infinitely ordered, is applied to a real system at a finite arbitrary rate. Part of this energy, regardless of its uniformity, does not convert to work on average over finite-time ensemble measurements. This is partly due to the random motions of particles inside the system to different directions at a given temperature — in absolute zero Kelvin the entropy is zero as there is no kinetic energy for random motions of particles. In this regard, external energy dissipates into different degrees of freedom in the form of heat at a given temperature. Therefore, even for an idealized thermodynamic system in which there is no other pathway for wasting energy such as friction or resistance, still part of the external energy dissipate into kinetic energies of particles and heat through random motions. In a broader picture, these random motions altogether emerge as a resultant force that opposes the external force on the boundary and across the system. The difference between the energy that is applied to the idealized system and the work that is done on the system is referred to as the entropy of that system. The usable energy which is the portion of energy that converts to work in an idealized system is realized as the free energy of the system. It is because of the entropy gain that the macroscopic state of the nonequilibrium system changes with time's arrow through an irreversible process. Evolving irreversible changes in a macroscopic system that is driven away from equilibrium under an applied external field are made of collective reversible microscopic fluctuations of degrees of freedom.

The thermodynamic properties such as entropy in a microscopic system under an applied external field can decrease or increase in a stochastic process through random fluctuations of microscopic degrees of freedom. Theses fluctuations in microscopic level which lead to probability distribution of entropy production with a symmetry around an average are recognized in fluctuation theorems (18; 19; 20; 21; 22; 23; 24; 25). The density probability distribution of entropy production exponentially narrows with the increase of the system's size and arrow of time. The average value resulted from these random fluctuations through arrow of time statistically increases the entropy of the macroscopic system (26; 27; 28; 29; 30; 31; 32).

In principle, it is possible that particles in a system experience fluctuation in the direction of the external field at the moment of collision for a given temperature. If particles of a system fluctuate in the same direction as an external force at the moment of collision the second law of thermodynamic will be violated as the work that is done on the system is more than the energy that is applied to it. However, the particles obtain various microstates and fluctuate stochastically in different directions owing to random Browning motions. As a consequence, the probability of such an event in a real system with an order of Avogadro number of atoms is statistically almost zero. However, it is a significantly probable event in an extremely small microscopic system with a single atom for a small fraction of time — work can be done one kT more than applied energy. This is a considerable contribution to the work when kT is comparable to the amount of applied energy. The violation of the second law of thermodynamics is recognized for such a microscopic system when the system contains only a few degrees of freedom for the creation of statistically averaged entropy for each measurement. With a huge number of degrees of freedom in a real macroscopic system, statistically, the system dissipates energy in the form of heat, and entropy increases with time under an applied external field. As a result, it is understood that the behavior of a system is governed by the energy and entropy of that system and its surrounding. But how about the distribution of particles within the system without an external field in thermal equilibrium with a heat reservoir? How the configuration of particles in the system is characterized by the energy and entropy of the equilibrium system?

The same principle applies to understanding the distribution of particles inside a system in thermal equilibrium with its infinite heat reservoir — the combination of the system and reservoir is considered as an isolated system. Similarly, in an equilibrated system, the energy and entropy affect the behavior of particles in the system. To understand and describe the effect of energy and entropy on the distribution of particles in an equilibrium system, we used a confined cubic box model as a closed system coupled with a reservoir. As it is expected, strong particle-particle interactions result in cluster formation, and strong particle-wall interactions result in the accumulation of a significant portion of particles in the vicinity of the walls. While energy contribution to the configuration of particles is deducible, the entropy contribution can be hidden since interaction forces interfere with entropic forces. What happens when there are no attraction energies in the system, and the energy effect is restricted to the repulsion of particles at contact?

Particles entropically are attracted to the walls as part of their excluded volume locate outside of the box, and as a consequence, the entropy increases. Therefore, when the volume of particles increases, the entropy contribution to the free energy becomes more effective, and entropic forces influence strongly the configuration of the particles in the system. The emergent attractive forces drive larger particles toward the walls. This effect is even more clear when particle-particle and particle-wall attractive forces are eliminated from the system. Such a system is realized for hard spheres in a box with reflective walls. In such a system, we can track the entropy effect on the system's search, through random motions, for a configuration of particles in which it gains the maximum microstates for degrees of freedom, and consequently, maximum entropy. In this regard, to elucidate the effect of entropy, we used a binary mixture of hard spheres in a box with reflective walls. The two-component system further allows us to understand the relationship between the volume of particles with configurational entropy by comparing how two types of particles with different volumes distribute in a box based on their entropy contributions to the system.

The number of accessible microstates for degrees of freedom maximizes when larger particles lay adjacent to the wall and smaller particles distribute in the remaining phase space. The system seeks a configuration in which some particles with degrees of freedom sacrifice their microstates for the collective increase in microscopic degrees of freedom of the whole system. Essentially, it is the accessible states for each degree of freedom that causes randomness in the motions of particles, and consequently, the mysterious concept of entropy. It is known that a time-evolving system favors a configuration that maximizes accessible states, and therefore, maximum entropy — until it reaches the equilibrium state from an initial given nonequilibrium configuration.

Lastly, our study emphasizes an emergent quasi-gravitational force on particles toward the walls of the box resulting from stochastic fluctuations of microscopic degrees of freedom in a process of maximizing entropy. As we show the attraction of particles to the wall does not require any fundamental attractive force in our molecular dynamics simulation, the emergent entropic force can be the foundation of gravity (33; 34; 35) and other fundamental forces owing to the fluctuation of all the possible microscopic degrees of freedom in phase space. This can be further elucidated by the incorporation of more components as a representation for other fundamental particles such as dark energy and dark matter into molecular computer simulations.

5 Conclusions

In this work, we used a mixture of particles in a box as a simple system to understand the entropy and energy effect on the distribution of particles. We showed that the configuration of particles in a box strongly depends on the entropic forces. We understood the entropy effect and depletion force using intuitive explanation, mathematical calculations, and molecular dynamics simulations. All evidence indicates, a system thrives to gain the maximum possible entropy based on the second law of thermodynamics. A system with only hard potentials which is realized in the binary mixture of hard spheres in a box with reflective walls favors large particles to lay next to the wall to minimize the excluded volume and maximize the residual space as so configurational entropy. Our work, emphasizes that attractive force can merely emerge from entropy as a consequence of random Browning motion of particles. The force from the boundaries of the system on larger particles comes from stochastic fluctuations of smaller particles in the system.

6 acknowledgement

We thank G.A.Parsafar for his discussions and intuition that contributed to this work during my master's degree (2010-2012) in physical chemistry at The Sharif University of Technology. We thank M.Rezaei for his assistance and discussion on this effort during our stay at The Sharif University of Technology. We thank the Advanced Computing Group of the University of Maine in particular Stephen Cousins for his continuous support and providing us with computer time.

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