Molecular Gravity and Phase Transition

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(Initial Version Published on June 16th, 2019)

Abstract

What holds molecules together in a solid and what causes it breaks apart in a phase transition? The van der Waals distance is defined as the distance between molecules at which the attraction and repulsion forces are balanced. At a smaller distance, the net force become repulsive. The volume of matters does prove the existence of repulsion between molecules, but cannot explain phase transition because this type of balance is maintained in all states: solid, liquid and gas. Molecular gravity proposed in this study provides the force to hold molecules together in a solid. Since the attraction and repulsion forces between molecules are balanced at van der Waals distance, the forces between molecules at a greater distance must be attractive. The effect of this attraction is similar to gravity, and so named molecular gravity. Molecular gravity becomes weaker as temperature increases. This should be a gradual process. However, the process is disruptive at phase transition in nature. What's the disruptive force? Orbital repulsion force is proposed to play a critical role in phase transition. Upon absorbing energy, an electron jumps to a higher orbital. The process not only increase the atom size of a molecule, but also reduces the distance to the adjacent molecules. Both processes increase the repulsion to the adjacent molecules. Because an orbital jump is spontaneous, the repulsion may exert a significant push to the adjacent molecules, causing vibrations of the molecules. As temperature increases, the repulsion force will eventually overcome molecular gravity and kick molecules apart: the phase transition.

Introduction

It is understood that phase transition is determined by intermolecular forces which in turn are affected by temperature and pressure. This study is intended to look into the details of these interactions. In particular, we will investigate two types of intermolecular forces: an attractive force named molecular gravity and a repulsive force named orbital repulsion. Their interactions determines phase transition.

Before moving forward, we need to clarify some nomenclature related to phase transition. An intermolecular force is the force which mediate interaction between molecules, including both attraction and repulsion forces. They are categorized into hydrogen bonding, ionic bonding, ion-induced dipole forces, ion-dipole forces and van der Waals forces. An intramolecular force is any force that binds together the atoms making up a molecule or compound, such as
covalent bonding and ionic bonding.\textsuperscript{[2-3]} By definition, these two terms should refer to two disjoint sets of forces. However, both claimed the ionic bonding, which make it somewhat confusion. At low temperatures, ions are held together in molecules by ionic bonds. However, at very high temperatures, such as in plasma, ions are separated. It is further confused with van der Waals force, which is sometimes used loosely for all intermolecular forces. The van der Waals force is a distance-dependent interaction between molecules, usually including Keesom force, Debye force, and London dispersion force.\textsuperscript{[4-6]} To avoid the confusion in our discussions, the term intermolecular force is used to refer to the definition: mediate interaction between molecules. Therefore, in a solid, an ionic bond is not count as intermolecular force. All these named forces are electrostatic in nature, which is described by Coulomb’s law:

\begin{equation}
F = Kq_1q_2r^{-2},
\end{equation}

where \( K \) is Coulomb’s constant, positive \( F \) is the repulsive force between signed charges \( q_1 \) and \( q_2 \), and \( r \) is the distance between the charges.\textsuperscript{[7-9]} It is an electric analogy to Isaac Newton’s universal gravitation.\textsuperscript{[10-11]} While gravity governs the interactions among celestial bodies in classical mechanics, Coulomb’s force is most prominent at the subatomic realm, which is \( 10^{36} \) magnitude stronger than the gravitational force.\textsuperscript{[12]}

**Molecular Gravity**

The concept of van der Waals radius was developed to recognize that atoms were not points.\textsuperscript{[13-14]} The van der Waals distance is defined as a distance between molecules that the intermolecular force becomes repulsive when distance between molecules is less than the van der Waals distance. At a greater distance, the force between molecules is attractive. In fact, the van der Waals radius is estimated based on the volume of gas. Half of the van der Waals distance is defined as van der Waals radius. In other words, it is the van der Waals radius that determine the volume of a system. The concept may be generalized to liquid and solid, which explains the volume and density of matter in general. The van der Waals distance is a balance point of repulsion and attraction forces between molecules. In response to a temperature change, both molecule size and van der Waals distance must be adjusted to find a new balance, which is observed as the thermal expansion. However, the balance between attraction and repulsion exists in all states of matter, which cannot explain phase transition.

To understand phase transition, interactions between multiple molecules must be considered collectively. Even though the attraction and repulsion forces are balanced between two adjacent molecules at van der Waals distance as shown by the red lines in Figure 1, the forces between molecules at a large distance (greater than the van der Waals distance) must be attractive as shown in the figure by the blue lines. Effect of these forces is somewhat like gravity, and so named molecular gravity. The force can be computed by integrating all the attractive forces from surrounding molecules. As a result, the repulsion between molecules is actually balancing the overall molecular gravity from surrounding molecules. Molecular gravity is always attractive, and therefore pulls molecules together. As modeled next, molecule size and distance between
molecules increase with temperature. The attractive force between molecules decreases with increasing temperature, and so does molecular gravity.

To see molecular gravity in action, let’s look at an example in ice crystal formation to understand why water is denser than ice. A water molecule consists of a single oxygen atom covalently bonded to two hydrogen atoms, or H-O-H.\textsuperscript{15} Because the oxygen nucleus is much larger than the hydrogen nucleus, it attracts and holds the two sharing electrons most of the time.\textsuperscript{18} The oxygen atom behaves like a negatively charged particle, while hydrogens positive. With the two hydrogen atoms forming an angle of 106.6\degree, the oxygen atom attracts hydrogen atoms from adjacent water molecules on the opposite side of the two hydrogen atoms, forming a hydrogen bond.\textsuperscript{17} Compared with a covalent bond, this is a weak bond. However, it dominates between water molecules at low temperatures and becomes critical in controlling and forming the less compacted crystal structure of ice, the hexagonal crystals also seen in snow flakes.\textsuperscript{18-22} The attraction of hydrogen bond exists not just in ice, but also in water. How can water molecules overcome the hydrogen bond and packed more densely? There is no shear resistance between water molecules. Without shear resistance, molecular gravity in water is like air pressure propagating evenly in all directions. Looking at a single hydrogen bond, molecular gravity not only exerts pressure in the direction of the bond, but also from the side. The bond just cannot support the greater molecular gravity surrounding it, but collapse and molecules pile up into a more compact packing. On the other hand, due to the fixed framework between ice molecules, multiple hydrogen bonds are scaffolded together to support molecular gravity, thus to produce a less compacted structure in ice and snow.

**Intermolecular Force**

To investigate intermolecular forces, we propose further scrutiny of the forces between molecules. Normally, each molecule is electrically neutral. However, it does not mean there is no electric force between molecules. Consider a model where electrons orbit around their nucleus in a cloud and the charge density is evenly distributed in the shells. The repulsion
against a negatively charged particle outside the atom can be computed by integrating the force over the shell. As a result, the accumulative repulsion from the shells is canceled exactly by the attraction of their nucleus, producing a zero net force to any charge outside the atom. This is not consistent with observations, because there are attractions holding molecules together in a solid. Then, how can we model the force between molecules? To establish a model, we need an accurate atom model in the first place. Unfortunately, a general solution to the Schrödinger equation is not available other than the hydrogen atom. Due to the dynamic nature of electrons, it is difficult to model intermolecular forces. Nevertheless, one thing we can do at least is to find the bounding values for the repulsion or attraction forces using a simplified model. Figure 2 shows two configurations for two helium atoms next to each other. The maximum repulsion force is found in configuration 2A and minimum in 2B. In configuration 2B, the two electrons orbital in the left atom is in a plane perpendicular to the centerline between the atoms.

![Figure 2](image)

**A, Maximum repulsion configuration**  
**B, Minimum repulsion configuration**

Figure 2, Configurations to model intermolecular forces using two helium atoms.

According to Coulomb’s law in equation (1), the net repulsion forces between the two atoms for configuration 2A and 2B are:

\[
F_a = Kq^2_e (s^2 + 6(s+2r)^2 + (s+4r)^2 - 4(s+r)^2 - 4(s+3r)^2),
\]

and

\[
F_b = Kq^2_e (4(s+2r)^2 - 2(s+r)^2 - 2(s+3r)^2 + 2(s+r)(r^2 + (r+s)^2)^{1.5} + 2(s+3r)(r^2 + (s+3r)^2)^{1.5} - 4(s+2r)(r^2 + (s+2r)^2)^{1.5}),
\]

where \(F_a\) and \(F_b\) are the maximum and minimum repulsion forces, \(K\) is the Coulomb’s constant, \(q_e\) is the charge of an electron, \(r\) is the radius of the helium atoms and \(s\) is the separation/distance between the two atoms. Using the model, we can investigate the repulsion trends in terms of atom sizes and distances between the atoms. For instance, given a helium atom radius 140 pm, Figure 3 depicts the repulsion trends as a function of atom distances. The maximum repulsion decreases quickly with increasing distance. It is interesting to note that the minimum repulsion has negative values, meaning there are attractions between the atoms in
configuration 2B. The attractions decrease with increasing distance. Both values approaches zero at infinite distance. It is important to understand that the two configurations are extreme cases. The repulsion force can be upto 5.4 nano N at a distance of 140 pm (one atom radius) and the attraction force can be upto 1.03 nano N. Since electrons are very dynamic particles, the actual configuration at any moment is something in between. So, for a given distance, the actual force must be a value between the two curves. Figure 3 also shows an important trend for the range between attraction and repulsion forces, which increases with decreasing distances between atoms. With a small distance, the range is very large. The value may fluctuate from repulsion to attraction. In other words, the force can be either repulsion or attraction and all depends on the actual configuration of the electron clouds.

**Figure 3, Maximum forces between two helium atoms as a function of distance.**

**Repulsion vs atom radius for distances 20, 30 and 40 pm**
It is also interesting to look into the repulsion trends as a function of atom sizes. The repulsion increases with atom sizes for a fixed atom distance. Three curves, blue, red and yellow, are plotted in Figure 4 for different distances, 20, 30 and 40 pm. In general, the repulsion increases with atom sizes for all the three distances. When atom size increases, the distance between the nucleus and electrons of adjacent atoms increases, which reduces the attractive components in equation (2) of the model.

Even though the above model is based on simple configurations between two helium atoms, the results can be generalized to most atoms/molecules, especially for large ones. Compared with helium, a hydrogen atom has only one proton and exerts less attraction to its electron. So, its atom size is larger. The model for hydrogen atoms produce similar trends, but with larger maximum repulsion/attraction ranges. The force modeled using helium and hydrogen represents the two extreme cases, where helium has fully filled in the outermost shell while hydrogen is minimally filled. For other elements, the force will be between the two models. With more electrons in large atoms, the repulsion between electrons causes them to be distributed more evenly in their shells. As mentioned earlier the evenly distributed electron clouds cancel the attraction from their nucleus to an outside electron. Hence, only the outermost electrons are significant to the force between atoms. So, the tends should be similar to either helium model or hydrogen model depending on the structure of the outermost orbitals.

At high temperatures, electrons move to higher orbitals, which effectively increases the atom sizes of molecules. Based on the results of the above model, repulsion increases with atom sizes. So, the repulsion between molecules increases with temperature. This is the mechanism of thermal expansion in general. It also explains that molecular gravity decreases as temperature increases.

**Orbital Repulsion Force**

Orbital repulsion was proposed to provide the driving force for the Crookes radiometer.[24] It is postulated that the force also play a critical role in phase transition. This is a spontaneous intermolecular force created in the process of orbital jump. After absorption of energy, an electron in an atom of a molecule jumps to a higher orbital.[25-26] Because an orbital jump is sudden, it may exert a repulsion force to an adjacent atom/molecule. As shown in Figure 5A, two single-atom molecules were next to each other with a small separation. On absorbing energy, one of the atoms goes through an orbital jump process, which increases the atom size and reduces the distance between them, Figure 5B. Both processes increased the repulsion between them, namely orbital repulsion.[24] The atoms were pushed apart and moved in opposite directions, Figure 5C. Based on the helium model above, the repulsion force can be significant at a close range. Orbital repulsion force may also be responsible for pushing molecules in Brownian motion.[27-28]
Phase Transition

Phase transition is the result of interaction between attraction and repulsion forces between molecules. It is postulated that molecular gravity provides the general attraction force to hold molecules together in solid at low temperatures. Particular bonds between molecules determine the crystal structures in solid, such as orientation of lattice. As shown in helium model, both molecular size and distance increase with temperature, which reduces the attraction, so does molecular gravity. This is a general trend and a gradual process. However, phase transition is a disruptive process. Orbital repulsion is postulated to provide the disruptive force in phase transition.

Figure 5, Orbital repulsion resulted from orbital jump.

Figure 6, Phase transition and intermolecular forces.
The state of matter is determined by the interaction of two forces: the orbital repulsion and molecular gravity in the absence of pressure. Pressure can be counted as a uniform attraction force in addition to molecular gravity. The three forces are shown in Figure 6B. Orbital repulsion increases with temperature shown as the orange curve, and molecular gravity in blue. Pressure is represented by the horizontal blue line. The net force between molecules are platted in a black curve. The net force is attractive at low temperatures, decreasing with increasing temperature, and becomes repulsive eventually.

In Figure 6A, the blue liquefying line is the transition from solid to fluid. At the transition, orbital repulsion $F_s$ breaks even with attraction/molecular gravity $F_g$ as shown in Figure 6B. At this point, orbital repulsion force is able to knock off the molecules from their crystal lattice. To the left of this point, molecular gravity is greater than orbital repulsion. The attraction is able to hold molecules together against the repulsion, where the orbital repulsion just pushes and increases the molecules oscillating. To the right, orbital repulsion overcomes molecular attraction. Molecules are kicked apart and solid breaks into fluid. The temperature at this point is the melting point, which does not change during the transition, indicating no increasing of potential energy. All the added energy is used to free up molecules and increase the kinetic energy of the molecules, which is where the latent heat goes.$^{[27]}$ In normal phase, the energy contribution to a system is divided between kinetic and potential energies, which increases both temperature and molecular vibrations. Temperature measures the level of potential energy, does not count for kinetic energy. This explains why heat capacity may vary for some substances because the energy may not split between kinetic and potential energy evenly.

Note, the net force may still be attractive to the right of the liquefying point. The force is not enough to hold against the orbital repulsion, but still provides the attraction between molecules to create viscosity in a fluid and surface tension on a liquid. The attraction is also responsible for capillary phenomenon, where liquid seems defying gravity. On surface of liquid or solid, orbital repulsion kicks/ejects molecules into the air, the processes known as vaporization or sublimation. Molecular attraction decreases with increasing temperature. At a temperature of supercritical point, Figure 6A, the attraction $F_p$ breaks even with repulsion $F_c$. Beyond this point, repulsion force is greater. There is no attraction force to provide viscosity between molecules in fluid. Because of that, there is no latent heat for the phase transition between liquid and gas beyond this point and the transition is not distinctive, a state known as supercritical fluid.$^{[29-30]}$

In a sense, pressure produces an additional attraction force to restraint molecules together. Liquid is just pressured gas. In fluid, as pressure increases, molecules are forced to stay at a closer distance. As pressure increases to a point, or the liquefying pressure, Figure 6A, intermolecular attraction becomes effective and is able to glue the molecules together into liquid. The liquefying pressure curves up with temperature because molecular repulsion increases with temperature. The liquefying curve does not extend beyond the critical point because there is no molecular attraction any more.
Conclusions

- Molecular gravity is a collective attraction force between molecules at a distance greater than the van der Waals distance. It provides the general attractive force to hold molecules together, such as solid at low temperatures.
- Orbital repulsion force is a short-ranged spontaneous force created during orbital jump. It pushes adjacent molecules apart, causing molecular vibrations. As temperature increases, the force will eventually overcome the attraction between molecules and knocks molecules off their crystal lattice, which is the liquefying phase transition.
- During phase transition, the energy of latent heat is all used to increase kinetic energy for freeing up molecules. There is no temperature change because potential energy is not increased.
- At low temperatures in fluid, the attraction force between molecules provides the viscosity. As temperature increases, the repulsion force eventually dominates. Without any attraction between molecules, there is no latent heat for phase transition, therefore no distinction between liquid and gas. The state is known as supercritical fluid.

References


