Breakdown of equipartition of energy for vibrational heat capacity of diatomic molecular gas due to nonvanishing bond length

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When the theorem of equipartition of energy applies to the vibrational degree of freedom within diatomic molecular gas, the bond length is usually taken as zero so that the theorem is valid. Once the bond length is taken into consideration, calculations show that the mean energy of the vibrational heat capacity will significantly deviate from the standard value near the high temperature which breaks the bond.

Keywords: equipartition of energy, vibrational degree of freedom, heat capacity, diatomic molecular gas, bond length

The theorem of equipartition of energy plays a crucial role in Boltzmann statistical mechanics or classical statistical mechanics, which states that molecules in thermal equilibrium have the same average energy associated with each independent degree of freedom of their motion and that the energy is $kT/2$, where $k$ is the Boltzmann constant and $T$ denotes the absolute temperature. For an ideal monatomic gas, the mean energy per molecule is $3kT/2$ for there are only three translational degrees of freedom. For an ideal diatomic molecular gas such as $H_2$, $O_2$ and $CO$ etc., there is a vibrational degree of freedom in which there is $kT/2$ coming from kinetic energy and $kT/2$ from potential energy, so it is usually claimed that the mean energy per molecule for each vibrational degree of freedom is $kT/2$. For a diatomic molecule, we take the harmonic approximation of the interaction between two atoms, and then we find that relative to one atom, another atom oscillates with a frequency around an equilibrium point, thus defining a bond length. For all diatomic molecules, the bond length between two atoms are finite, for instance, for $H_2$, $O_2$ and $CO$ gas, it is 74, 148, 143 picometers, respectively. To note that the so-called bond energy is characterized by $m(ωr_0)^2/2$, where $m$ is the reduced mass, $ω$ is the vibrational frequency and $r_0$ is the bond length. An important situation appears at dissociation temperature $T_d$ determined by $kT_d ≈ m(ωr_0)^2/2$; the bond breaks and the diatomic molecule will be dissociated. Once the bond length is effectively taken as zero, the theorem of equipartition of energy is valid.

The present study demonstrates how equipartition of energy for vibrational potential energy with a nonvanishing bond length can be seriously deviated from $kT/2$ at high temperature. For simplicity, we confine ourselves to an ideal model of the diatomic molecule without considering the non-harmonic oscillations, nor accounting for the non-separability between rotational and vibrational degrees of freedom of the molecule near dissociation temperature $T_d$.

Partition function for vibrational potential energy within a diatomic molecule gas is usually given by,

$$Z_{vp}^1 = \int_{-\infty}^{\infty} \exp\left(-\frac{1}{2} \beta m \omega^2 r^2\right) dr = \sqrt{\frac{\pi}{2 \beta m \omega^2}},$$  \hspace{1cm} (1)

where $\beta = 1/kT$. The mean vibrational potential energy $u_{vp}$ per molecule is,

$$u_{vp} = -\frac{\partial}{\partial \beta} \ln Z_{vp}^1 = \frac{1}{2} kT.$$  \hspace{1cm} (2)

It is right the theorem of equipartition of energy for the vibrational potential energy.

Now, we take the finite bond length $r_0$ into consideration, we have the partition function for the vibrational potential energy,

$$Z_{vp}^1 = \int_0^{\infty} \exp\left(-\frac{1}{2} \beta m \omega^2 (r - r_0)^2\right) dr = \sqrt{\frac{\pi}{\beta m \omega^2}} \left(\text{erf}\left(\frac{r_0 \sqrt{\beta m \omega^2}}{\sqrt{2}}\right) + 1\right),$$  \hspace{1cm} (3)

where erf $(x)$ is the error function defined by,

$$\text{erf} (x) \equiv \frac{2}{\sqrt{\pi}} \int_0^x \exp (-t^2) dt.$$  \hspace{1cm} (4)

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Two immediate consequences or remarks follow. First, defining a temperature dependent length parameter $l_T$,

$$l_T \equiv \sqrt{\frac{2}{\beta m \omega^2}} \sim \sqrt{kT}, \quad (5)$$

we find that $l_T \approx r_0$ amounts to $T \approx T_d$, so a reasonable interval of temperature is $T \in (T_i, T_d)$ where $T_i$ is the liquefaction temperature which is determined by experiments or theoretical calculations. In present study, we do not care much about the precise value of this temperature $T_i$ which can be simply taken as zero Kelvin without affecting our conclusion.

Secondly, the mean distance between two atoms are in fact of temperature dependence via,

$$\bar{r} = \frac{1}{Z_1^{vp}} \int_0^\infty r \exp\left(-\frac{1}{2} \beta m \omega^2 (r - r_0)^2\right) dr = r_0 + \frac{l_T \exp\left(- \frac{(r_0)}{l_T} \right)^2}{\sqrt{\pi} \left( \text{erf} \left( \frac{r_0}{l_T} \right) + 1 \right)} = r_0 + r_T, \quad (6)$$

and the mean of the square of the distance is,

$$\bar{r}^2 = \frac{1}{Z_1^{vp}} \int_0^{\infty} r^2 \exp\left(-\frac{1}{2} \beta m \omega^2 (r - r_0)^2\right) dr = r_0^2 + r_0 r_T + \frac{l_T^2}{2}, \quad (7)$$

where,

$$r_T = \frac{l_T \exp\left(- \frac{(r_0)}{l_T} \right)^2}{\sqrt{\pi} \left( \text{erf} \left( \frac{r_0}{l_T} \right) + 1 \right)}. \quad (8)$$

The square root of the average value of standard deviation of the distance $r$, or the fluctuation of the distance, is defined by $\Delta r \equiv \sqrt{\bar{r}^2 - \bar{r}}$ which is given by,

$$\Delta r = \sqrt{\frac{l_T^2}{2} - r_0 r_T - r_T^2}. \quad (9)$$

In whole temperature interval $T = (0, T_d)$, the mean distance $\bar{r}$ remains almost unchanged as $r_T/r_0 \approx (0, 0.113)$, but it is not the case for the fluctuation of the distance as $\Delta r/r_0 \approx (0, 0.612)$ from which we see that as $T \to T_d$, the distance between two atoms fluctuates dramatically. In other words, it is the fluctuation of the distance $\Delta r$ rather than the elongated mean distance $\bar{r}$ cuts the bond as temperature $T$ reaches $T_d$. Results of the fluctuation of the distance $\Delta r$ are plotted in FIG.1.

With the partition function $Z_1^{vp} [3]$, the mean vibrational potential energy is,

$$u^{vp} = -\frac{\partial}{\partial \beta} \ln Z_1^{vp} = \frac{1}{2} k T \left( 1 - \frac{2 x \exp(-x^2)}{\sqrt{\pi} (3 - \text{erf}(x))} \right), \quad (10)$$

where $x \equiv r_0/l_T$, and $x \approx 1$ when $T \approx T_d$. When $T < T_d$, $x \gg 1$, the exponent function $\exp(-x^2)$ becomes much smaller, so the equipartition value is recovered,

$$u^{vp} \approx \frac{1}{2} k T. \quad (11)$$

The greatest deviation from the equipartition value $kT/2$ appears at $x \approx 0.778$, at which $u^{vp} = 0.394 kT < 0.5 kT$; and at $T \approx T_d$, $u^{vp} = 0.403 kT < 0.5 kT$. It is sufficiently to conclude that the theorem of equipartition of energy is not applicable near the dissociation temperature. Nevertheless, a more striking result is available from examining the heat capacity $c^{vp} \equiv \partial u^{vp}/\partial T$, which is simply,

$$\frac{c^{vp}}{k} = \frac{1}{2} \left( 1 - \frac{x e^{-x^2} (2 x^2 + 1)}{\sqrt{\pi} (1 + \text{erf}(x))} - \frac{2 e^{-2x^2} x^2}{\pi (1 + \text{erf}(x))} \right). \quad (12)$$

The standard result is $c^{vp} = 0.5 k$; and ours is smaller. The biggest deviation occurs at $x \approx 0.974 \approx 1$, i.e., $T \approx T_d$, and we have $c^{vp} = 0.318 k < 0.5 k$. In other words, when the temperature is so high as $T \approx T_d$, i.e., $x \approx 1$, which suffices to break the bond, the theorem of equipartition of energy is seriously violated. The result given by Eq. (12)
is plotted in FIG. 2. However, the theorem of equipartition of energy is in fact valid in an ordinary condition which is easily accessible in laboratories.

Take $O_2$ gas for instance. The basic data are listed in the following $[6]$. The reduced mass of the oxygen molecule $m = 1/2 \ast 2.657 \ast 10^{-26}$ kg, and vibrational frequency $\omega = 4.66 \times 10^{13}$, and bond length $r_0 = 148$ picometers. The dissociation temperature is $24548K$. At room temperature $T = 300K$, $\beta = 7.2 \times 10^{22} J^{-1}$, we have $l_T = 17.0$ picometers which lead to correction to the bond length by an addition amount of small distance $r_T \simeq 5.82 \ast 10^{-21}$ picometers, too bit to be meaningful. In opposite limit at the temperature $T = 90.K$ at which the oxygen gas starts to liquefy $[6]$, no deviation from the theorem of equipartition of energy is observable as well.

The present study can be summarized in the following. A universal result is identified for the vibrational heat capacity of the diatomic gas does not obey the equipartition of energy at high temperature domain due to the nonvanishing bond length. It is understandable in the following senses. Because the theorem states that the mean value of every independent quadratic term in the Hamiltonian is equal to $kT/2$, and only if all terms in the Hamiltonian are quadratic then the mean energy is spread equally over all degrees of freedom. This theorem says nothing about the possible contributions from other non-quadratic terms in the Hamiltonian, and they really have. One familiar example is the heat capacity resulted from non-harmonic oscillations in crystal.

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FIG. 1: The fluctuation of the distance between two atoms as $\Delta r$ in unit bond length $r_0$ (solid line) and the mean distance $\bar{r}$ in unit $r_0$ (dashed line, plotted as contrast) versus the ratio $l_T/r_0 \sim \sqrt{kT}$. Results show that the value of $\bar{r}$ changes a little, but that of $\Delta r$ changes dramatically. Though these curves are meaningful only within temperature interval $(T_l, T_d)$ in which $T_l$ is finite, we can also simply assume $T_l \simeq 0$ at which the theorem of equipartition of energy starts to apply.

FIG. 2: The heat capacity $c^{vp}$ in unit Boltzmann constant $k$ from the vibrational potential energy (solid line) and the mean vibrational potential energy $u^{vp}$ in unit $kT$ (dashed line, plotted as contrast) versus the ratio $x \equiv r_0/l_T \sim \sqrt{\beta}$. Results show that at relatively low temperature, the theorem of equipartition of energy holds true, but becomes worse as $T \to T_d$. The same caution of the applicable temperature interval $(T_l, T_d)$ as that specified in FIG. 1 applies.