Renormalization and heat capacity for anharmonicity

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Anharmonic oscillator plays important roles in two distant area, one is in the classical mechanics in which it exhibits renormalization of the bare frequency, and another is in the statistical mechanics in which it causes a correction to the vibrational contribution of the heat capacity of an ideal gas of diatomic molecules. The heat capacity correction and the renormalized value of the bare frequency share a common characteristic quantity due to the higher order perturbations to the harmonic motion.

Keywords: renormalization, nonlinearity, statistical mechanics, anharmonic oscillator.

I. INTRODUCTION

For an anharmonic oscillator, the frequency consists of two parts. One is bare and intrinsic, depending on the material parameters such as mass and spring constant and all irrespective of its state in oscillating or not, and another is normalized and extrinsic, depending on much energy input into the system and what the phase of the oscillation and all determined by the external influences. Once presence of the anharmonicity, the bare frequency needs to be renormalized to remove the superficial divergence, or precisely, to eliminate the secular term that grows as time increases. On the other hand, the anharmonicity plays crucial roles in microscopic world, such as physical properties of solid, and the heat capacity of an ideal gas of diatomic molecules. The deterministic Newtonian mechanics and probable statistical mechanics are deeply intertwined and the relationship in between has been a fundamental problem explored more than one century and half, since the Boltzmann time 1 to date, 2 but there are still important issues that remain not yet fully understood. After quite a long time research, a novel relationship between the renormalization in quantum field theory and removal of the secular term in perturbation expansion has been uncovered, and many relevant advances have been made, 4–12 but all limited to the quantum field theory. It is curious that both the quantum field theory and the statistical mechanics starts from the similar mathematical quantity, the path integrals in quantum field theory and partition function in statistical mechanics, but so far there is no relation between the renormalized value and the heat capacity had been found. The present paper explores whether the renormalized value of the bare frequency or the bare frequency itself possibly appears in the partition function thus produces the possible experimentally testable effect in the heat capacity. For that first glance these two quantities are far distant, because the renormalized frequency depends on the oscillation amplitude that is determined by the amount of energy input into the oscillator, but the partition function takes account for all possible microstates accessible to the system. In present article, we show the renormalized frequency and the corrections to the heat capacity depend on the same characteristic quantity.

In diatomic molecules, there is the equilibrium distance between the two nuclei, denoted by \( r = r_0 \) at which the potential \( U (r) \) is minimum \( dU/dr = 0 \). When vibrations with large quantum numbers are excited, the anharmonicity of the vibrations and their interaction with the rotation of the molecule may become important, and these effects are in principle of the same order of magnitude. 3 Landau and Lifshitz demonstrated that anharmonicity of the vibrations between two nucleus in the molecule takes the following form, 3

\[
U (r) = U (r_0) + \frac{1}{2} m \omega_0^2 \left( (r - r_0)^2 - \frac{\alpha}{r_0^3} (r - r_0)^3 + \gamma \frac{r_0}{r^4} (r - r_0)^4 \right)
\]

where, \( m \) is the reduced mass, and \( \omega_0 \) is the bare spring constant, and \( \alpha \) and \( \gamma \) are two dimensionless constants can be expressed in terms of the spectroscopic constants of the molecule, 3 and, \( \xi \equiv r/r_0 - 1 \). Since the vibrational quantum numbers are so large such the vibrations and the rotation of the molecule are coupled, the corresponding correction to the thermodynamic quantities may be determined classically. 3

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The "bare" solution of the first order equation of motion is, 

\[
\frac{d^2 r}{dt^2} = -\omega_0^2 (r - r_0) - \frac{3}{2} \frac{\alpha}{r_0} (r - r_0)^2 + 2 \frac{\gamma}{r_0^3} (r - r_0)^3
\]  

(2)
i.e.,

\[
\frac{d^2 \xi}{dt^2} = -\omega_0^2 \left( \xi - \frac{3}{2} \frac{\alpha}{r_0} \xi^2 + 2 \frac{\gamma}{r_0^3} \xi^3 \right) = -\omega_0^2 \xi + \frac{3}{2} \left( \omega_0^2 \alpha \right) \frac{\xi^2}{r_0} - 2 \left( \omega_0^2 \gamma \right) \frac{\xi^3}{r_0^3}
\]  

(3)
The standard scheme of the Poincare–Lindstedt method is first to rewriting the bare frequency \( \omega_0 \) in term \( \omega_0^2 \xi \) as \( \omega^2 \xi - (\omega^2 - \omega_0^2) \xi \) in which the new frequency \( \omega \) is the correct one and \( (\omega^2 - \omega_0^2) \xi \) is called the counter-term in the quantum field theory. \[4 \] Landau’s form of potential \( U(r) \) \[11\] suggest a convenient utilization of the Poincare–Lindstedt method in the following, which is to assume that bare frequency \( \omega_0 \) in the first equation \[3\] is modified, so the correct equation of motion takes the following form, accurate up to \( O(\gamma) \) or \( O(\alpha^2) \),

\[
\frac{d^2 \xi'}{dt^2} \approx - (\omega_0 + \omega_1 + \omega_2)^2 \left( \xi' - \frac{3}{2} \frac{\alpha}{r_0} \xi' + 2 \frac{\gamma}{r_0^3} \xi'^3 \right)
\]  

(4)
where,

\[
\xi' \approx \xi_0 + \xi_1 + \xi_2.
\]  

(5)
where \( \omega_1 \sim O(\alpha) \) and \( \omega_2 \sim O(\alpha^2) \) are both small and so are \( \xi_1 \sim O(\alpha) \) and \( \xi_2 \sim O(\alpha^2) \), \( \omega_0, \omega_1, \) and \( \omega_2 \) are the zeroth, first and second order of frequency, and so for \( \xi_0, \xi_1 \) and \( \xi_2 \) of the reduced position \( \xi' \).

The zeroth order equation of motion is,

\[
\frac{d^2 \xi_0}{dt^2} + \omega_0^2 \xi_0 = 0, \quad \xi_0(0) = A, \quad d\xi_0(0)dt = 0,
\]  

(6)
where \( A \) is the amplitude of the unperturbed oscillator. The first order equation of motion is,

\[
\frac{d^2 \xi_1}{dt^2} = \left( \xi_1(t) - \frac{1}{2} \omega_0^2 (2 \xi_1(t) - 3a \xi_0(t)) + 4 \omega_0 \omega_1 \xi_0(t) \right) = 0,
\]  

(7)
together with the initial conditions \( \xi_1(0) = 0, \ d\xi_1(0)dt = 0 \). The second order equation of motion is,

\[
\xi''_2(t) + \omega_0^2 \xi_2(t) + \left( 2 \omega_0 \omega_1 - 3a \omega_0^2 \xi_0(t) \right) \xi_1(t) + 2b \omega_0^2 \xi_0(t)^3 - 3a \omega_0 \omega_1 \xi_0(t)^2 + 2 \omega_0 \omega_2 \xi_0(t) + \omega_0^2 \xi_0(t) = 0,
\]  

(8)
together with the initial conditions \( \xi_2(0) = 0, \ d\xi_2(0)dt = 0 \).

The zeroth order equation of motion give the usual harmonic oscillating solution,

\[
\xi_0 = A \cos (\omega_0 t).
\]  

(9)
The "bare" solution of the first order equation of motion is,

\[
\xi_1(t) = -\omega_1 tA \sin (\omega_0 t) + \frac{1}{2} \frac{\alpha}{r_0} A^2 \sin \left( \frac{\omega_0 t}{2} \right) \left( \frac{3 \sin \left( \frac{\omega_0 t}{2} \right) + \sin \left( \frac{3\omega_0 t}{2} \right)}{2} \right).
\]  

(10)
The first term gives the divergent oscillating amplitude \( \omega_1 tA \) as time \( t \to \infty \) with \( \omega_1 \neq 0 \). To remove the divergence, we must choose,

\[
\omega_1 = 0.
\]  

(11)
The corrected first order solution of equation of motion (11) is,

\[ \xi_1(t) = \frac{1}{2} \frac{\alpha}{\gamma_0} A^2 \sin \left( \frac{\omega_0 t}{2} \right) \left( \left( 3 \sin \left( \frac{\omega_0 t}{2} \right) + \sin \left( \frac{3\omega_0 t}{2} \right) \right) \right). \]  

(12)

The "bare" solution of the second order equation of motion is,

\[ \xi_2(t) = \frac{1}{16} \left( 3A^2 \omega_0 \left( 5 \left( \frac{\alpha}{\gamma_0} \right)^2 - 4 \left( \frac{\gamma}{\gamma_0} \right) \right) - 16\omega_2 \right) \sin(\omega_0 t) \]  

(13)

\[ -A^3 \sin^2 \left( \frac{\omega_0 t}{2} \right) \left( \frac{11}{8} \left( \frac{\alpha}{\gamma_0} \right)^2 + \frac{1}{4} \left( \frac{\gamma}{\gamma_0} \right)^2 \right) \cos(\omega_0 t) \]  

(14)

\[ -A^3 \sin^2 \left( \frac{\omega_0 t}{2} \right) \left( \frac{35}{16} \left( \frac{\alpha}{\gamma_0} \right)^2 + \frac{1}{4} \left( \frac{\gamma}{\gamma_0} \right) \right) + \left( \frac{3}{16} \left( \frac{\alpha}{\gamma_0} \right)^2 + \frac{1}{4} \right) \cos(2\omega_0 t) \). \]  

(15)

The first term gives also the divergent oscillating amplitude as time \( t \to \infty \), but this divergence can be simply removed with \( \omega_2 \) so chosen to satisfy,

\[ \left( 3A^2 \omega_0 \left( 5 \left( \frac{\alpha}{\gamma_0} \right)^2 - 4 \left( \frac{\gamma}{\gamma_0} \right) \right) - 16\omega_2 \right) = 0. \]  

(16)

It amounts to the second order correction of the frequency \( \omega_2 \) to be,

\[ \omega_2 = \frac{A^2}{2\gamma_0} \left( \frac{15}{8} \alpha^2 - \frac{3}{2} \gamma \right) \omega_0. \]  

(17)

The corrected second order solution of equation of motion (11) is,

\[ \xi_2(t) = -\frac{A^3}{\gamma_0^2} \sin^2 \left( \frac{\omega_0 t}{2} \right) \left( \frac{35}{16} \alpha^2 + \gamma + \left( \frac{11}{8} \alpha^2 + \frac{1}{2} \gamma \right) \right) \cos(\omega_0 t) \]  

(18)

\[ + \left( \frac{3}{16} \alpha^2 + \frac{1}{4} \right) \cos(2\omega_0 t) \right). \]  

(19)

The important result for our purpose is the bare frequency \( \omega_0 \) to be renormalized to be,

\[ \omega = \omega_0 + \frac{A^2}{2\gamma_0} \left( \frac{15}{8} \alpha^2 - \frac{3}{2} \gamma \right) \omega_0, \]  

(20)

where the modified part \( \omega_2 \) depends on the external parameter \( A \). However, the characteristic quantity \( \chi \) in it is,

\[ \chi = \frac{15}{8} \alpha^2 - \frac{3}{2} \gamma. \]  

(21)

It is anticipated that only this quantity appears at statistical mechanics.

It is interesting to explore the energy of oscillation in the presence of the anharmonicity. The oscillation is composed of a single prime frequency \( \omega_0 \) and its higher harmonics,

\[ \xi' \approx A \cos(\omega_0 t) + \frac{1}{2} \frac{\alpha}{\gamma_0} A^2 \sin \left( \frac{\omega_0 t}{2} \right) \left( \left( 3 \sin \left( \frac{\omega_0 t}{2} \right) + \sin \left( \frac{3\omega_0 t}{2} \right) \right) + \right) \]  

(22)

\[ -\frac{A^3}{\gamma_0^2} \sin^2 \left( \frac{\omega_0 t}{2} \right) \left( \frac{35}{16} \alpha^2 + \gamma + \left( \frac{11}{8} \alpha^2 + \frac{1}{2} \right) \right) \cos(\omega_0 t) + \left( \frac{3}{16} \right) \cos(2\omega_0 t) \right), \]

and the energy is,

\[ E = \frac{1}{2} m \left( \frac{d\xi'}{dt} \right)^2 + U(r). \]  

(23)

Explicitly, the mean value is given by, accurate up to \( O(\gamma) \) or \( O(\alpha^2) \),

\[ E \approx \frac{1}{2} m (\omega_0 A)^2 \left( 1 - \frac{A}{\gamma_0} + \left( \frac{15}{8} \right) \left( \frac{A}{\gamma_0} \right)^2 \right). \]  

(24)
It amounts to both the frequency and amplitude of the oscillation are modified in the following way,

\[ A' = A \left( 1 - \frac{\alpha A}{2r_0} - \frac{(\alpha^2 - 4\gamma)}{2} \left( \frac{A}{2r_0} \right)^2 \right). \]  

(25)

In consequence, the energy can then be rewritten as,

\[ E \approx \frac{1}{2} m (\omega A')^2. \]  

(26)

The energy shift is thus,

\[ \Delta E = E - \frac{1}{2} m (\omega_0 A)^2 = \frac{1}{2} m (\omega_0 A)^2 \left( \frac{\alpha A}{r_0} - \chi \left( \frac{A}{r_0} \right)^2 \right). \]  

(27)

It depends on both \( A \) and \( \chi \).

III. THE ANHARMONICITY INDUCED CORRECTION OF THE HEAT CAPACITY

The configurational part of the vibrational partition function takes the following form, with setting \( U(r_0) = 0 \),

\[
Z_U = \frac{1}{r_0} \int_0^{\infty} \exp(-\beta U(r)) dr \\
= \int_{-1}^{\infty} \exp \left( -\beta \left( \frac{1}{2} m \omega_0^2 \right) \xi \right) \left( \xi^2 - \alpha \xi^3 + \gamma \xi^3 \right) d\xi \\
\approx \int_{-1}^{\infty} \exp \left( -\frac{\xi^2}{\rho} \right) \left( 1 + \frac{\alpha \xi - \gamma \xi^4}{\rho} + \frac{1}{2} \left( \frac{\alpha \xi^3}{\rho^2} \right)^2 \right) d\xi
\]  

(28)

where

\[
\rho \equiv \frac{1}{\beta m \omega_0^2 r_0^2} = \frac{2k_B T}{m \omega_0^2 r_0^2}
\]  

(29)

should be much small than unity for \( r_0 \) is approximately the length of the bond between two molecules, and once the temperature is so high such that \( k_B T \approx (1/2) m \omega_0^2 r_0^2 \), the thermal energy breaks the bond the diatomic molecule no longer exists. The result of the integral is,

\[
Z_U = \frac{1}{2} \alpha e^{-1/\rho} (\rho + 1) + \frac{\sqrt{\pi}}{2} \left( \text{erf} \left( \sqrt{\frac{1}{\rho}} \right) + 1 \right) \\
+ - \gamma \left( 3 \sqrt{\pi} \left( \text{erf} \left( \sqrt{\frac{1}{\rho}} \right) + 1 \right) \frac{1}{8} \left( \frac{1}{\rho} \right)^{3/2} - \frac{1}{4} e^{-1/\rho} (3\rho + 2) \right) \\
+ \frac{1}{32} \alpha^2 \left( 15 \sqrt{\pi} \left( \text{erf} \left( \sqrt{\frac{1}{\rho}} \right) + 1 \right) \frac{1}{8} \left( \frac{1}{\rho} \right)^{3/2} - 2 e^{-1/\rho} (5\rho (3\rho + 2) + 4) \right)
\]  

(30)

where \( \text{erf} \left( x \right) = \frac{2}{\sqrt{\pi}} \int_0^x \exp \left( -t^2 \right) dt \) is the error function. The first few terms in asymptotic expression of \( \text{erf} \left( x \right) \) when \( x \gg 1 \) is useful,

\[
\text{erf} \left( x \right) \approx 1 - \frac{e^{-x^2}}{x \sqrt{\pi}} \left( 1 - \frac{1}{2x^2} + \frac{3}{(2x^2)^2} \right).
\]  

(31)

We have the partition function,

\[
Z_U \approx F + Ge^{-1/\rho},
\]
where,
\[ F = \frac{1}{16} \sqrt{\pi} \rho \left( 15 \alpha^2 \rho - 12 \gamma \rho + 16 \right), \]
\[ G = -\frac{\alpha^2}{4 \rho} + \frac{1}{8} \left( 4 \alpha - 5 \alpha^2 + 4 \gamma \right) - \frac{1}{16} \left( 8 - 8 \alpha + 15 \alpha^2 - 12 \gamma \right) \rho + O(\rho^{3/2}). \]

Since \( \rho \ll 1 \), \( e^{-1/\rho} \approx 0 \), we have,
\[ Z_U \approx \sqrt{\pi \rho} \left( 1 + \frac{3}{16} \left( 5 \alpha^2 - 4 \gamma \right) \rho \right). \]

The first term comes from the unperturbed oscillator. The configurational part of the vibrational free function is,
\[ F_U \approx -N k_B T \ln Z_U = -N k_B T \ln \left( \sqrt{\pi \rho} \left( 1 + \frac{1}{2} \left( \frac{15}{8} \alpha^2 - \frac{3}{2} \gamma \right) \rho \right) \right) \]
\[ = -N k_B T \ln \sqrt{\pi \rho} - N k_B T \ln \left( 1 + \frac{1}{2} \left( \frac{15}{8} \alpha^2 - \frac{3}{2} \gamma \right) \rho \right) \]
\[ \approx -N k_B T \ln \sqrt{\pi \rho} - \frac{1}{2} N k_B T \rho \left( \frac{15}{8} \alpha^2 - \frac{3}{2} \gamma \right). \]

The anharmonicity induces correction to the vibrational free function is,
\[ \Delta F_U \approx -\frac{1}{2} N k_B T \rho \left( \frac{15}{8} \alpha^2 - \frac{3}{2} \gamma \right) = -N k_B T \frac{1}{2} \left( \frac{15}{8} \alpha^2 - \frac{3}{2} \gamma \right) \rho. \]

Landau and Lifshitz calculated this quantity but obtained a seriously wrong result, in our notation, 
\[ -N k_B T \frac{1}{4} (1 + 3 \alpha) \rho - N k_B T \frac{1}{4} \left( \frac{15}{8} \alpha^2 - \frac{3}{2} \gamma \right) \rho. \]

It is clear that, the correction to the vibrational free function is closely related to renormalization of the frequency, but irrespective of the external parameter \( A \). The resultant correction to the internal energy is,
\[ \Delta U_U \approx -\frac{1}{2} \left( \frac{15}{8} \alpha^2 - \frac{3}{2} \gamma \right) \rho \frac{\partial}{\partial \beta} \rho = N \chi \frac{(k_B T)^2}{m \omega_0^2 n_0} = N k_B T \frac{1}{2} \chi \rho. \]

The corresponding correction to heat capacity is,
\[ \Delta C = \frac{\partial \Delta U}{\partial T} = N k_B \rho \chi. \]

IV. CONCLUSIONS

For anharmonic oscillator, the frequency must be renormalized to eliminate the secular term that grows as time increases. However, the frequency depends on the external parameter and a characteristic quantity defined in present work. Since the anharmonic oscillator emerges in the diatomic molecules, it is interesting to explore the renormalized frequency or the other quantity may appear in heat capacity of an ideal gas of the diatomic molecules. Results show that there is a characteristic quantity defined via the renormalized frequency which depends on both intrinsic and extrinsic quantities. The renormalized value of frequency does not appear directly in the statistical mechanics.

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