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MODIFICATION OF THE DEBYE THEORY OF SPECIFIC HEAT DUE TO NON-EXTENSIVE STATISTICS

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By allowing for a multi-fractal distribution for the population densities of the states of a harmonic oscillator we demostrate that the thermal average energy of a quantizied harmonic oscillator receives a correction due to the non-extensive statistics of Tsallis. By applying this result to the phonon spectrum we show that this in turn generates an anomalous correction to the Debye formula for the specific heat of a solid at low temperatures.

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1. Introduction

The fact that configurations of condensed matter as well as cosmological structures admit fractal or multi-fractal structures has increasingly become realized in the past two decades [1–3]. The universe, usually thought to be homogeneous and isotropic over large scales, has revealed a self-similar structure on smaller scales [4], and in fact all microscopic systems with long range interactions and non-Markovian memory [5] have proved to admit a multi-fractal structure requiring a statistical treatment beyond the usual Boltzmann-Gibbs approach and quantum statistical approach. The introduction of the non-extensive statistics of Tsallis [6] involves generalizing the Boltzmann-Gibbs entropy and takes into account the multi-fractal relationship of the energy levels of a system with respect to one another. Subsequent applications of this idea to the solar plasma [7–9] have proven to cut-off the high energy tail of the Maxwell–Boltzmann distribution and lead to the production of solar neutrinos in accord with experimental finding of solar neutrino production. Along with these studies, applications to a generalized H theorem [10–12], the fluctuation dissipation theorem [13], the Langevin and Fokker–Planck equation [14], the classical equipartition theorem [15], the Ising chain [16,17] paramagnetic systems [18] and the Planck radiation law [19,20], have lead to measurable corrections to the usual treatment in terms of the non-extensive parameter $q \neq 1$. In cosmology, the non-extensive statistics of Tsallis leads to a modification of the primordial helium abundance that can be parametrized in terms of $(q-1)$ [21]. In the present note, we consider the states of the quantized harmonic oscillator to be distributed in a multi-fractal manner, and apply Tsallis statistics to calculate the average thermal energy of a single "phonon mode" of frequency ν. We then use this average energy to calculate the total thermal energy of the lattice vibrations, which in turn leads to modifications of the Debye theory of specific heat at low temperatures [22]. Since lower and lower temperatures are being probed in low temperature physics [23], limits on modifications of the specific heat due to non-extensive statistics might very well be established if the corrections can be singled out.

2. *Non-extensive statistics and the Debye theory of specific heat*

We begin by writing the entropy of an ensemble of N identical systems (or particles) using the non-extensive statistics of Tsallis,

$$S = \frac{kN}{q-1}\left(1 - \sum P_i^q\right) = k\sigma N\,, \tag{2.1}$$

where $P_i = N_i/N$, q is nonextensive statistics parameter and σ is the dimensionless entropy of a single particle. In the present problem, the non-extensive statistics is applied to the states of a single particle system. Equation (2.1) can be written as

$$S = \frac{kN}{q-1}\left(\sum P_i - \sum P_i^q\right) \qquad \left(P_i = \frac{N_i}{N}\right)\,, \tag{2.2}$$

where we vary Eq. (2.2) with respect to N_i, along with the constraints

$$\sum N_i = constant\,, \tag{2.3}$$

$$\sum N_i \varepsilon_i = constant\,.$$

We find upon using the Lagrangian multipliers μ/τ and $-1/\tau$ (μ is the chemical potential,

$\tau = kT$, T is the absolute temperature and k is the Boltzmann constant)

$$N_i = \frac{N}{q^{1/(q-1)}} \left(1 + \frac{\mu - \varepsilon_i}{\tau}\,(q-1)\right)^{1/(q-1)}, \tag{2.4}$$

$$N_i = \frac{N}{q^{1/(q-1)}}\ \exp\left\{\frac{1}{q-1}\ln\left(1+\frac{\mu-\varepsilon_i}{\tau}(q-1)\right)\right\},$$

giving for $(q-1)$ small

$$N_i = \frac{N}{q^{1/(q-1)}}\ \exp\left(\frac{\mu-\varepsilon_i}{\tau} - \frac{(\mu-\varepsilon_i)^2}{2\tau^2}(q-1)\right), \tag{2.5}$$

To find μ, we expand $\mu = \mu_0 + \alpha\mu_1 + \alpha^2\mu_2$, where $q-1 = \alpha$ is a small parameter. Further, we have

$$\frac{1}{q^{1/(q-1)}} = \frac{1}{(1+\alpha)^{1/\alpha}} = \frac{1}{\mathrm{e}^{\ln((1+\alpha)/\alpha)}} \cong \frac{1}{\mathrm{e}^{(\alpha-\alpha^2/2)/\alpha}} \cong \mathrm{e}^{-1}\left(1+\frac{\alpha}{2}\right). \tag{2.6}$$

(to first order in α), and finally

$$\frac{1}{q^{1/(q-1)}} = \mathrm{e}^{-1}\left(1+\frac{\alpha}{2}\right).$$

When we insert the expansion for $\mu = \mu_0 + \alpha\mu_1 + \ldots$ and Eq. (2.6) into Eq. (2.5), we find

$$N_i = \frac{N}{\mathrm{e}}\left(1+\frac{\alpha}{2}\right)\mathrm{e}^{(\mu_0-\varepsilon_i)/\tau}\left(1+\frac{\alpha\mu_1}{\tau}\right)\left(1-\frac{(\mu_0-\varepsilon_i)^2\alpha}{2\tau^2}\right), \tag{2.7}$$

or

$$N_i = \frac{N}{\mathrm{e}}\mathrm{e}^{(\mu_0-\varepsilon_i)/\tau} + \frac{\alpha N}{\mathrm{e}}\mathrm{e}^{(\mu_0-\varepsilon_i)/\tau}\left(\frac{1}{2}+\frac{\mu_1}{\tau}\,\frac{(\mu_0-\varepsilon_i)^2}{2\tau^2}\right). \tag{2.8}$$

When we sum Eq. (2.8) using $\sum N_i = N$, we have to zeroth and first order for the states of a simple harmonic oscillator ($\varepsilon_i = (i+1/2)\hbar\omega$)

$$\mathrm{e}^{(\mu_0/\tau)} = \frac{\mathrm{e}}{\sum_{i=0}^{\infty}\mathrm{e}^{(\varepsilon_i/\tau)}} = \mathrm{e}\frac{\mathrm{e}^{(\hbar\omega/\tau)}-1}{\mathrm{e}^{(\hbar\omega/\tau)}}, \tag{2.9}$$

$$\mu_1 = -\frac{\tau}{2} + \frac{1}{2\tau}\frac{\sum \mathrm{e}^{(\mu_0-\varepsilon_i)/\tau}(\mu_0-\varepsilon_i)^2}{\sum \mathrm{e}^{(\mu_0-\varepsilon_i)/\tau}}.$$

Thus

$$\mu_0 = \tau\ln\mathrm{e} + \tau\ln\left(\mathrm{e}^{\hbar\omega/\tau}-1\right) + \tau\mathrm{e}^{-\hbar\omega/2T} \tag{2.10}$$

$$\simeq \tau + \hbar\omega - \hbar\omega/2 \simeq \hbar\omega/2 \qquad \text{for} \qquad \hbar\omega/\tau \gg 1\,.$$

For μ_1 we have

$$\mu_1 = -\frac{\tau}{2} + \frac{\mu_0^2}{2\tau} - \frac{\mu_0}{\tau}\left(\frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\hbar\omega/\tau} - 1}\right) \tag{2.11}$$

$$+\frac{1}{2\tau}\left(\frac{e^{\hbar\omega/\tau} - 1}{e^{\hbar\omega/\tau}}\right)\left(\frac{1}{4} + \frac{\tau}{\hbar\omega} + 2\left(\frac{\tau}{\hbar\omega}\right)^2\right)(\hbar\omega)^2\,.$$

In evaluating Eq. (2.9), we used

$$\sum e^{-\varepsilon_i/\tau} = \frac{e^{\hbar\omega/2\tau}}{e^{\hbar\omega/\tau} - 1}\,,$$

$$\frac{\sum \varepsilon_i e^{-\varepsilon_i/\tau}}{e^{-\varepsilon_i/\tau}} = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\hbar\omega/\tau} - 1}\,,$$

$$\sum \varepsilon_i^2 e^{-\varepsilon_i/\tau} \qquad (i = n)$$

by the integral

$$\int_0^\infty \varepsilon_n^2 e^{-\varepsilon_n/\tau} dn = (\hbar\omega)^2 \int_0^\infty (n + \frac{1}{2})^2 e^{-(n+1/2)\hbar\omega/\tau} dn$$

$$= (\hbar\omega)^2 \int_{1/2}^\infty x^2 e^{-x\hbar\omega/\tau} dx = (\hbar\omega)^2 e^{-\hbar\omega/2\tau}\left(\frac{1}{4} + \frac{\tau}{\hbar\omega} + 2\left(\frac{\tau}{\hbar\omega}\right)^2\right)\,.$$

For $\hbar\omega/\tau \gg 1$,

$$\mu_1 \simeq -\frac{\tau}{2} + \frac{(\hbar\omega)^2}{8\tau} - \frac{(\hbar\omega)^2}{4\tau} + \frac{(\hbar\omega)^2}{8\tau} = -\frac{\tau}{2}\,. \tag{2.12}$$

Thus,

$$\mu_0 = \frac{\hbar\omega}{2}, \qquad \mu_1 = -\frac{\tau}{2}, \qquad \text{for} \qquad \hbar\omega/\tau \gg 1\,.$$

For the average thermal energy, we have from Eq. (2.8)

$$\bar{\varepsilon} = \frac{1}{N}\sum N_i \varepsilon_i = \frac{1}{N}\sum N e^{-1} e^{(\mu_0 - \varepsilon_i)/\tau} \varepsilon_i \tag{2.13}$$

$$= \alpha e^{-1} \sum_i \left(\frac{\varepsilon_i}{2} + \frac{\mu_1 \varepsilon_i}{\tau} + \left(\frac{\mu_0 - \varepsilon_i}{2\tau^2}\right)^2 \varepsilon_i\right) e^{(\mu_0 - \varepsilon_i)/\tau}\,.$$

Using $e^{\mu_0/\tau} = e/(\sum e^{-\varepsilon_i/\tau})$, and $\mu_1 = -\tau/2$ in Eq. (2.13), we have

$$\bar{\varepsilon} = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\hbar\omega/\tau} - 1} - \frac{\alpha}{2\tau^2} \frac{\sum e^{-\varepsilon_i/\tau}(\mu_0 - \varepsilon_i)^2 \varepsilon_i}{\sum e^{-\varepsilon_i/\tau}}. \tag{2.14}$$

Again in Eq. (2.14), if we replace the sums $\sum \varepsilon_n^2 e^{-\varepsilon_n/\tau}$ and $\sum \varepsilon_n^3 e^{-\varepsilon_n/\tau}$ by

$$\int_0^\infty \varepsilon_n^2 e^{(n+\frac{1}{2})\hbar\omega/\tau}\, dn \to \frac{\hbar\omega}{2}^2 \int_{1/2}^\infty x^2 e^{-x\hbar\omega/\tau}\, dx$$

and

$$\int_0^\infty \varepsilon_n^3 e^{(n+\frac{1}{2})\hbar\omega/\tau}\, dn \to \frac{\hbar\omega}{2}^3 \int_{1/2}^\infty x^3 e^{-x\hbar\omega/\tau}\, dx$$

we find for Eq. (2.14)

$$\bar{\varepsilon} = \left(1 - \frac{\alpha\mu_0}{2\tau^2}\right)\left(\frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\hbar\omega/\tau} - 1}\right)$$

$$\frac{e^{(\hbar\omega/\tau)} - 1}{e^{(\hbar\omega/\tau)}} \left[\alpha\mu_0 \left(\frac{\hbar\omega}{\tau}\right)^2 \left(\frac{1}{4} + \frac{\tau}{\hbar\omega} + 2\left(\frac{\tau}{\hbar\omega}\right)^2\right)\right. \tag{2.15}$$

$$\left. -\frac{\alpha}{2\tau^2}(\hbar\omega)^3 \left(\frac{1}{16} + \frac{3}{4}\left(\frac{\tau}{\hbar\omega}\right) + 3\left(\frac{\tau}{\hbar\omega}\right)^2 + 6\left(\frac{\tau}{\hbar\omega}\right)^3\right)\right]$$

Again, for$\hbar\omega/\tau \gg 1$, Eq. (2.15) becomes

$$\bar{\varepsilon} = \left(\frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\hbar\omega/\tau} - 1}\right)\left(1 - \frac{\alpha}{8}\left(\frac{\hbar\omega}{\tau}\right)^2\right) + \frac{2}{32}\alpha\frac{(\hbar\omega/\tau)^3}{\tau^2}. \tag{2.16}$$

We have obtained the result Eq. (2.16) in a previous note [24], but in that discussion we only considered the specific heat of a single mode ω (Einstein model of specific heat) [25]. We now multiply Eq. (2.16) by $3\omega^2/(2\pi^2 V_0^3)d\omega$, which is the number of modes of phonon excitations between ω and $\omega + d\omega$ (per unit volume), where there are three polarization states and the speed of sound in the solid is V_0 (Ref. 22). We also note that $3N = \omega_M^3/(2\pi^2 V_0^3)$, where N is the number of atoms per unit volume. For the totoal energy of the lattice vibrations, we have

$$U = \int_0^{\omega_M} \left(\frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\hbar\omega/\tau} - 1}\right)\left(1 - \frac{\alpha}{8}\left(\frac{\hbar\omega}{\tau}\right)^2\right)\left(\frac{3\omega^2}{2\pi^2 V_0^3}\right) d\omega \tag{2.17}$$

$$+\frac{3}{32}\alpha\int_0^{\omega_M}\frac{(\hbar\omega)^3}{\tau^2}\left(\frac{3\omega^2}{2\pi^2V_0^3}\right)\mathrm{d}\omega\,.$$

If we subtract off the vacuum energy from Eq. (2.17), we get from that equation

$$U=\frac{3\hbar}{2\pi^2V_0^3}\int_0^{\omega_M}\frac{\omega^3\mathrm{d}\omega}{e^{\hbar\omega/\tau}-1}-\alpha\int\frac{(\hbar\omega)^3}{\tau^2(e^{\hbar\omega/\tau}-1)}\left(\frac{3\omega^2}{16\pi^2V_0^3}\right)\mathrm{d}\omega \tag{2.18}$$

$$+\alpha\int_0^{\omega_M}\frac{3}{64}\frac{(\hbar\omega)^3}{\tau^2}\frac{\omega^2\mathrm{d}\omega}{\pi^2V_0^3}\,.$$

The first term in Eq. (2.18) represents the usual term, and the other two are corrections due to the non-extensive statistics. Letting $\hbar\omega/\tau = x$ in the first two terms of Eq. (2.18), we have

$$U=\frac{3\tau^4}{2\pi^2\hbar^3V_0^3}\int_0^{x_M}\frac{x^3\mathrm{d}x}{e^x-1}-\frac{3\alpha\tau^4}{16\pi^2V_0^3\hbar^3}\int_0^{x_M}\frac{x^5\mathrm{d}x}{e^x-1}+\frac{\alpha\hbar^3\omega_M^6}{128\pi^2V_0^3\tau^2}\,. \tag{2.19}$$

For very low T, we may let $x_M\to\infty$ giving

$$U=T^4\left(\frac{3k^4}{2\pi^2\hbar V_0^3}\frac{\pi^4}{15}-\frac{K_0\alpha k^4(3)}{16\pi^2\hbar^3V_0^3}\right)+\frac{\beta}{\tau^2}=\gamma T^4+\frac{\beta}{T^2}\,. \tag{2.20}$$

where

$$K_0=\int_0^{x_M}\frac{x^3\mathrm{d}x}{e^x-1},\qquad \beta=\frac{\alpha\hbar^3\omega_M^6}{128\pi^2V_0^3k^2}\,,$$

γ is the coefficient of T^4 in Eq. (2.20), ω_M is given by $3N=\omega_M^3/(2\pi^2V_0^3)$, and $\tau = kT$. For the specific heat, we have per unit volume (N atoms per unit volume)

$$C_V=\left(\frac{\partial U}{\partial T}\right)=4\gamma T^3-\frac{2\beta}{T^3}\,. \tag{2.21}$$

The first term in Eq. (2.21) represents the Debye formula (with the modified coefficient) for the specific heat [26], while the second term represents a negative $1/T^3$ correction that increases with decreasing T. Here the correction term will change the curvature of C_V vs. T for decreasing T at low T. Two points should be made concerning the above calculations, firstly, the assumption $\hbar\omega/\tau\gg 1$, used in evaluating Eqs. (2.10) and (2.11) breaks down for low ω. However, if the first discrete mode of ω is such that $\hbar\omega>\tau$, the replacement of the discrete sum by the integral in Eq. (2.17) is justified and the assumption $\hbar\omega/\tau\gg 1$ valid in Eqs. (2.10) and (2.11). The second points that in Eq. (2.20), the second term is assumed small compared to the first term, thus below a certain critical T, Eq. (2.21) is no longer valid. The essential point is that when the corrections are taken into account, a small lowering of C_V varying as $1/T^3$ will be a signature of non-extensive statistics in the phonon spectrum.

3. Conclusion

The result in Eq. (2.21) predicts corrections to the Debye theory that are unlike any corrections predicted by improving on mode counting due to the discrete nature of the lattice waves. The usual formula $3\omega^2/(2\pi^2 V_0^3)\,\mathrm{d}\omega$ for the number of modes between ω and $\omega + \mathrm{d}\omega$ receives its first correction as $b_4\omega^4\,\mathrm{d}\omega(b_4 = const)$ [27]. This in turn generates a correction to C_V that varies as T^5. This implies that any corrections to C_V that decrease C_V at low T with a characteristic curvature of $1/T^3$ would be suggestive of the presence of anomalous statistics operative in the phonon spectrum or lattice wave spectrum. Another feature of the curve of C_V vs. T that would reveal anomalous statistical effects is the fact that the coefficient of the T^3 term in C_V would be diminished below that predicted by the Debye theory as expressed in Eq. (2.20) for U. Since extremely low temperature measurements of C_V would yield very small values of C_V, it would be most feasible to search for anomalous deviations from the T^3 behaviour at temperatures exceeding 100 K. The known deviation (Ref. 22, p. 126) of the predicted values of C_V from the experimental value of C_V at 100 K is about 1.4% for silver, which suggests that more precise measurements might be capable of identifying the presence of anomalous statistical effects giving rise to a correction which is of the order of a percent or less.

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PROMJENA DEBYEVE TEORIJE SPECIFIČNE TOPLINE U NEEKSTENZIVNOJ STATISTICI

Pretpostavi li se višefraktalna raspodjela gustoće popunjenosti stanja harmoničkog oscilatora, pokazuje se da, prema Tsallisovoj neekstenzivnoj statistici, prosječna toplinska energija kvantiziranog oscilatora prima popravku. Primjenom tog ishoda na fononski spektar, dobiva se anomalna popravka Debyevog izraza za specifičnu toplinu čvrsnine na niskim temperaturama.