Non-extensive Study of Rigid and Non-rigid Rotators

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Abstract

The isotropic rigid and non-rigid rotators in the framework of Tsallis statistics are studied in the high and low temperature limits. The generalized partition functions, internal energies and heat capacities are calculated. Classical results of the Boltzmann-Gibbs statistics have been recovered as non-extensivity parameter approaches to 1. It has also been observed that non-extensivity parameter q behaves like a scale parameter in the low temperature regime of the rigid rotator model.

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I. INTRODUCTION

The non-extensive generalization of the standard Boltzmann-Gibbs statistics was proposed in 1988 by C. Tsallis[1-4]. This non-extensive generalization begins with the supposition of a new, fractal inspired entropy $S_q \equiv k(1-\sum_i p_i^q)/(q-1)$ where q is any real number and k is a positive constant which becomes Boltzmann constant in the limit q→ 1. In this case, the new entropy S_q takes the form $-k_B \sum_i p_i \ln p_i$, which is simply the standard entropy formula.This new non-extensive statistics has been studied a great deal to list its properties and it is also applied to many well-known examples of the Boltzmann-Gibbs statistics such as Ehrenfest theorem[5], Fokker- Planck equations[6] and quantum statistics[7].

We first calculate the partition function of the isotropic rigid rotator for both high energy and low energy limits and then obtain the generalized internal energy and specific heat expressions for both cases. This forms the Section II. The usual Maxwell-Boltzmann results are obtained in the limit q→ 1. In Section III, we turn our attention to non-rigid rotator and follow the same procedure for it as in the Section II. Results and discussions are given in Section IV.

II. ISOTROPIC RIGID ROTATOR

Energy levels of a rigid rotator are[8]

$$E_j = j(j+1)\hbar^2/2\mu a^2. \tag{1}$$

where j=0,1,2, ..., $\mu = m_1 m_2/(m_1+m_2)$ reduced mass of the nuclei and a being the equilibrium distance between them.The degeneracy of each level is $g_j = 2j+1$. In non-extensive formalism (NEXT), the partition function is given by

$$Z_q = \sum_{j=0}^{\infty}(2j+1)[1-\frac{\beta(1-q)j(j+1)\hbar^2}{2\mu a^2}]^{1/(1-q)}. \tag{2}$$

Setting $\theta = \hbar^2/2ma^2k$, then we get

$$Z_q = \sum_{j=0}^{\infty}(2j+1)[1 - \frac{(1-q)j(j+1)\theta}{T}]^{1/(1-q)}. \quad (3)$$

Now we are ready to look for its analytic solutions in the high and low temperature limits.

i)High temperature limit

At high temperatures, $\frac{\theta}{T} \ll 1$ and [1-$\frac{(1-q)j(j+1)\theta}{T}$]$^{1/(1-q)}$ changes slowly as j changes. So we take it as a continuous function of j. Letting j(j+1)=x and substituting (2j+1)dj=dx, then, we have

$$Z_q = \int_0^{\infty} dx[1 - \frac{(1-q)x\theta}{T}]^{1/(1-q)}. \quad (4)$$

For the interval $1 \langle\, q \,\langle\, 2$, solution to the above integral is

$$Z_q = \frac{T}{\theta}\frac{1}{2-q}. \quad (5)$$

As q goes to 1, we get

$$Z_{q\to 1} = \frac{T}{\theta}. \quad (6)$$

The expression above is exactly the Maxwell-Boltzmann (MB) partition function for the isotropic rigid rotator in the high temperature limit. Thus, we calculate the generalized internal energy function from

$$U_q = -\frac{\partial}{\partial\beta}\frac{Z_q^{1-q}-1}{1-q}, \quad (7)$$

in the non-extensive case. It becomes

$$U_q = \frac{1}{\beta^2}[\frac{\alpha}{(2-q)}\beta^{-1}]^{-q}\frac{\alpha}{(2-q)}\ , \qquad 1\langle q\langle 2 \quad (8)$$

where $\alpha \equiv \frac{1}{k\theta}$. It is important to see that again, in the limit when q approaches to 1, we obtain the result already known in MB statistics, i.e.,

$$U_{q\to 1} = \frac{1}{\beta} = k_B T. \quad (9)$$

It is also possible to calculate the specific heat in this statistics as

$$C_q = \frac{\partial U_q}{\partial T}, \quad (10)$$

where U_q is the internal energy function. We immediately get

$$C_q = (\frac{\alpha}{2-q})^{1-q} \frac{1}{k^{q-2}} (2-q) T^{1-q}. \quad (11)$$

As q$\longrightarrow$ 1, $C_q \longrightarrow k_B$ is verified easily. All these calculations are carried out by using the constraint $\sum_{i=1}^{W} p_i^q \varepsilon_i = U_q$. But, this choice of internal energy constraint presents several difficulties. For example, the probability distribution obtained by using this constraint is not invariant under uniform translation of the energy spectrum. Another important consequence of this constraint is that it leads to violation of energy conservation macroscopically.The solution to all these difficulties are recently proposed by C. Tsallis et al. [9]. They introduced the new internal energy constraint as follows

$$\frac{\sum_{i=1}^{W} p_i^q \varepsilon_i}{\sum_{i=1}^{W} p_i^q} = U_q. \quad (12)$$

This choice of constraint remedied all previous difficulties. Since we have studied all thermodynamical quantities with the previous internal energy constraint, we must reconsider them with this new constraint. There are two ways to do this: Firstly, we can recalculate all thermodynamical quantities with this new internal energy constraint by forming the new partition function. Another method is to find the relation between the temperature parameters of the old and new calculations. If one has all thermodynamical functions calculated with the old constraint and the relation between temperature parameters is known, it is possible to modify all previous calculations carried out with the constraint $\sum_{i=1}^{W} p_i^q \varepsilon_i = U_q$. This is the method we will follow, because we already have the solutions with respect to old constraint.

We begin by writing all previous calculations in terms of intermediate variable t' where $t' \equiv 1/(\beta' \varepsilon)$. From now on, The superscript (2) will refer to calculations done by old constraint.

The partition function of the rigid rotator in the high temperature limit becomes

$$Z_q^{(2)}(\beta') = \frac{T'}{\theta}\frac{1}{(2-q)} = \frac{t'}{(2-q)}. \tag{13}$$

Thus, we first evaluate the denominator in the Eq.(12)

$$\sum_j [p_j^{(2)}(\beta')]^q = \sum_j \frac{[1-(1-q)\beta'\varepsilon_j]^{q/(1-q)}}{Z_q^{(2)q}}. \tag{14}$$

or it is explicitly written as

$$\sum_j [p_j^{(2)}(\beta')]^q = \frac{(2-q)^q}{t'^q}\sum_j [1-(1-q)\beta'\varepsilon_j]^{q/(1-q)}. \tag{15}$$

By defining

$$\sum_j [1-(1-q)\beta'\varepsilon_j]^{q/(1-q)} = t', \tag{16}$$

we write it in the following simple form

$$\sum_j [p_j^{(2)}(\beta')]^q = (2-q)^q (t')^{1-q}. \tag{17}$$

We now proceed by using the mathematical relation between β and β' which is

$$\beta = \beta' \frac{\sum_j [p_j^{(2)}(\beta')]^q}{1-(1-q)\beta' U_q^{(2)}(\beta')/\sum_j [p_j^{(2)}(\beta')]^q}. \tag{18}$$

Substituting Eq. (17) into the Eq. (18), we get

$$t' = (2-q)^{(q+1)/q} t^{1/q}. \tag{19}$$

From Ref. [9], we have

$$Z_q'^{(3)}(\beta) = Z_q^{(2)}(\beta'). \tag{20}$$

By mere substitution, we get

$$Z_q'^{(3)}(\beta) = (2-q)^{1/q} t^{-1/q}. \tag{21}$$

We also have

$$p_j^{(3)}(\beta) = p_j^{(2)}(\beta'). \tag{22}$$

Thus, we formed $p_j^{(3)}(\beta)$. Next, we use the relation

$$\sum_j [p_j^{(3)}(\beta)]^q = (\bar{Z}_q^{(3)})^{1-q}, \tag{23}$$

to obtain the partition function

$$(\bar{Z}_q^{(3)})^{1-q} = (2-q)^{1/q} t^{(1-q)/q}. \tag{24}$$

Therefore, one may obtain internal energy and heat capacities by using the following relation

$$\beta \frac{\partial U_q^{(3)}}{\partial \beta} = \frac{\partial}{\partial \beta}(\ln_q \bar{Z}_q^{(3)}). \tag{25}$$

We find

$$U_q^{(3)} = (2-q)^{1/q} t^{1/q}, \tag{26}$$

where $ln_q x \equiv \frac{x^{1-q}-1}{1-q}$. Heat capacity is given by

$$C_q^{(3)} = \frac{dU_q^{(3)}}{dT} = \frac{k}{q}(2-q)^{1/q} t^{(1-q)/q}. \tag{27}$$

Again, as $q \longrightarrow 1$, $C_q^{(3)} \longrightarrow k_B$ is obtained. This is the rotational specific heat of the isotropic rigid rotator for high temperature limit in accordance with the equipartition theorem. Finally, we plot $C_q^{(3)}$ in terms of reduced temperature $t=T/\theta$ in Fig. 1.

ii) Low temperature limit

At low temperatures, if q is small enough concerning the non-extensive (1-q) part, we have $T \ll \theta$. We look at first few terms of the summation in the Eq. (3)

$$Z_q^{(2)} \cong 1 + 3[1 - 2(1-q)\frac{\theta}{T}]^{1/(1-q)}. \tag{28}$$

This is nothing but the well-known partition function of the rigid rotator in low temperature limit in MB statistics if (1-q) is small enough. This is the case if we make q closer to 1. For such a choice, the partition function takes the form

$$Z_{q \longrightarrow 1}^{(2)} \cong 1 + 3\exp(-2\theta/T). \tag{29}$$

The generalized internal energy function for this case becomes

$$U_q^{(2)} = \frac{6}{\alpha}[1+3[1-2(1-q)\frac{\beta}{\alpha}]^{1/(1-q)}]^{-q}[1-2(1-q)\frac{\beta}{\alpha}]^{q/(1-q)}. \tag{30}$$

This is a relatively long expression for the internal energy function but if we look at the q$\rightarrow$ 1 limit again, we see that it is of the form

$$U_{q\rightarrow 1}^{(2)} = \frac{6k_B\theta}{Z_{q\rightarrow 1}}\exp(-2\theta/T), \tag{31}$$

with $1/\alpha = k_B\theta$ in the q$\rightarrow$ 1 limit. Calculation of the specific heat reads

$$\begin{aligned} C_q^{(2)} = & \frac{12q}{\alpha^2 kT^2}[1+3[1-2(1-q)\frac{\beta}{\alpha}]^{1/(1-q)}]^{-q}[1-2(1-q)\frac{\beta}{\alpha}]^{\frac{2q-1}{1-q}} \\ & -\frac{36q}{\alpha^2 kT^2}[1+3[1-2(1-q)\frac{\beta}{\alpha}]^{1/(1-q)}]^{-q-1}[1-2(1-q)\frac{\beta}{\alpha}]^{\frac{2q}{1-q}}. \end{aligned} \tag{32}$$

To modify the equations above in accordance with the third constraint, we substitute the Eq. (19) into the Eq. (3) and take the first two terms to get the low temperature limit partition function

$$Z_q^{(3)} \cong 1+3[1-2(1-q)(2-q)^{-(q+1)/q}\theta^{1/q}T^{-1/q}]^{1/(1-q)}. \tag{33}$$

Using this partition function, we immediately get the specific heat value as

$$\begin{aligned} C_q^{(3)} = & \frac{6k}{t^{1/q}}(2-q)^{-(q+1)/q}[1+3(1-2(1-q)(2-q)^{-(q+1)/q}t^{-q})^{1/(1-q)}]^{-q} \\ & [1-2(1-q)(2-q)^{-(q+1)/q}t^{-q}]^{q/(1-q)}. \end{aligned} \tag{34}$$

As $q \longrightarrow 1$, it reduces to

$$C_q^{(3)} \longrightarrow \frac{12}{\alpha^2 k_B T^2}\exp(-2\theta/T). \tag{35}$$

This limiting value of heat capacity is obtained by observing that $\frac{1}{Z_{q\longrightarrow 1}^{(3)}}$ is almost equal to unity for low temperature partition function values. This consideration also holds for Eq. (33)

The plots related to low temperature case are illustrated again in terms of the reduced temperature in Fig. 2. The interesting feature in these plots is that specific heat function of the rigid rotator in the low temperature regime attains the same shape as the classical one but with a narrower width and a shift in the peak to the left. By increasing q, specific heat function attains the same shape as the classical one but with a narrower width and a shift in peak to the left.

III. ISOTROPIC NON-RIGID ROTATOR

In this case, energy levels are given by[10]

$$E_j^{(nonrigid)} = \frac{\hbar^2}{2I_0} j(j+1) - \frac{\hbar^4}{2I_0^2 k R_0^2} j^2(j+1)^2. \tag{36}$$

where $I_0 = \mu R_0^2$ and k is spring constant. We have neglected the third order term $j^3(j+1)^3$ in the above expression. It is better to rewrite equation above in the simple form

$$\bar{E}_j^{(nonrigid)} = \frac{E_j^{(nonrigid)}}{hc} = Bj(j+1) - Dj^2(j+1)^2. \tag{37}$$

where D is called centrifugal distortion constant. The first term on the right hand side simply corresponds to the rigid rotator part which had been studied in detail in the previous section, and non-rigidity term is explicitly given as, apart from a multiplicative factor which is very small compared to the rigidity part factor, $j^2(j+1)^2$. The partition function in the NEXT formalism reads

$$Z_q^{(nonrigid)} = \sum_{j=0}^{\infty} (2j+1)[1-\beta(1-q)\bar{E}_j^{(nonrigid)}]^{1/(1-q)}. \tag{38}$$

By substituting the related energy equation to the equation above, we get

$$Z_q^{(nonrigid)} = \sum_{j=0}^{\infty} (2j+1)[1-\beta(1-q)Bj(j+1) + \beta(1-q)Dj^2(j+1)^2]^{1/(1-q)}. \tag{39}$$

We again look for its solutions in the high and low temperature limits.

i)High temperature limit

We make the same assumptions used in the the rigid rotator case.

$$Z_q^{(nonrigid)} = \int_0^{\infty} dx[1-\beta(1-q)Bx + \beta(1-q)Dx^2]^{1/(1-q)}, \tag{40}$$

or simply

$$Z_q = \int_0^\infty dx[ax^2 + bx + 1]^{1/(1-q)}. \tag{41}$$

where

$$a = \beta(1-q)D \quad and \quad b = -\beta(1-q)B. \tag{42}$$

The integral above can be rewritten in factorial form

$$Z_q = (mn)^{\frac{1}{1-q}} \int_0^\infty dx(x + \frac{1}{m})^{1/(1-q)}.(x + \frac{1}{n})^{1/(1-q)}, \tag{43}$$

where $m = b - n$ and $n = \frac{b}{2}\ [1 \pm (1 - 4\frac{a}{b^2})^{1/2}]$. We shall use the following general form to evalute the above integral

$$\int_0^\infty dxx^{\nu-1}(x+\beta)^{-\mu}(x+\gamma)^{-\sigma} = \beta^{-\mu}\gamma^{\nu-\sigma}\ Beta(\nu, \mu-\nu+\sigma)_2F_1(\mu, \upsilon; \mu+\sigma; 1-\frac{\gamma}{\beta}), \tag{44}$$

where $\mu = \frac{1}{q-1}$, $\nu = 1$, $\gamma = \frac{1}{n}$ and $\beta = \frac{1}{m}$. ${}_2F_1(\rho, \mu; \gamma; x)$ is the hypergeometric function given below

$${}_2F_1(\rho, \mu; \gamma; x) = \frac{\Gamma(\gamma)}{\Gamma(\mu)\Gamma(\gamma-\mu)} \int_0^1 dtt^{\mu-1}(1-t)^{\gamma-\mu-1}(1-xt)^{-\rho}, \tag{45}$$

where the parameters satisfy $\nu > 0$ and $\mu > \nu - \sigma$. Here we see that $\nu = 1$ and $q > 1$. Thus, we simply get

$$\mu = \sigma = \frac{1}{q-1}. \tag{46}$$

By using the condition $\mu > \nu - \sigma$, we obtain an upper limit for q as $q < 3$. Therefore, we have a solution range for q as $1 < q < 3$. Thus we get the partition function as

$$Z_q = \frac{(q-1)}{(3-q)n}\ {}_2F_1(1, 1/(q-1); 2/(q-1); 1-\frac{m}{n}). \tag{47}$$

. In order to get the compact expression for the partition function above, we made use of the following identity:

$$Beta(1, \frac{2}{q-1} - 1) = \frac{q-1}{3-q}. \tag{48}$$

The resulting internal energy and heat capacity expressions may be found by using Equations (7) and (10) respectively together with the partition function above.Variation of heat capacity in the high temperature limit is plotted in Fig. 3. In all the plots related to non-rigid rotator, we have used 10.397 and 4.1×10^{-5} as B and D parameters respectively for HCl molecule [11].

ii) Low temperature limit

As in the case for isotropic rigid rotator in the low temperature limit, we look at first few terms of the summation in the Eq. (39)

$$Z_q \cong 1 + 3[1 - 2B(1-q)\beta + 4D(1-q)\beta]^{\frac{1}{1-q}}. \tag{49}$$

Internal energy term resulting from the partition function above is

$$U_q = 6(B-2D)[1+2(B-2D)(q-1)\beta]^{\frac{q}{1-q}}[1+3(1+2(B-2D)(q-1)\beta)^{\frac{1}{1-q}}]^{-q}. \tag{50}$$

The specific heat function of non-rigid rotator for this case is illustrated in Fig. 4, with using B and D constants for HCl molecule, 10.397 and 4.1×10^{-5} again.

IV. RESULTS AND DISCUSSIONS

We have studied isotropic rigid and non-rigid rotators in the non-extensive statistics by extending the previous work on anisotropic rigid rotator[12]. We have calculated heat capacity at high and low temperature limits for each rotator. At high temperature, results are in well agreement with classical cases. We also observe some interesting features for low temperature case. There happens to be shift to the left in the zeros of internal energy functions by increasing q as is plotted in Fig. 2. By increasing q from 1 to 3/2, specific heat function preserves the same shape as the q=1 case but with a narrower width and a shift to the left. One of the interesting features of Tsallis statistics is that in the limiting Tsallis index, i.e. as q$\rightarrow$ 1, one gets the corresponding Maxwell-Boltzmann result at once. This has also been true for the partition functions, generalised energy functions and specific heats in the high and low temperature limits of the isotropic rigid rotator. We have concluded that study of extensive systems through non-extensive thermostatistics bears importance[13].

V. ACKNOWLEDGEMENTS

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FIGURES

FIG. 1. Specific heat of the rigid rotator as a function of reduced temperature t=T/θ in the high temperature limit.

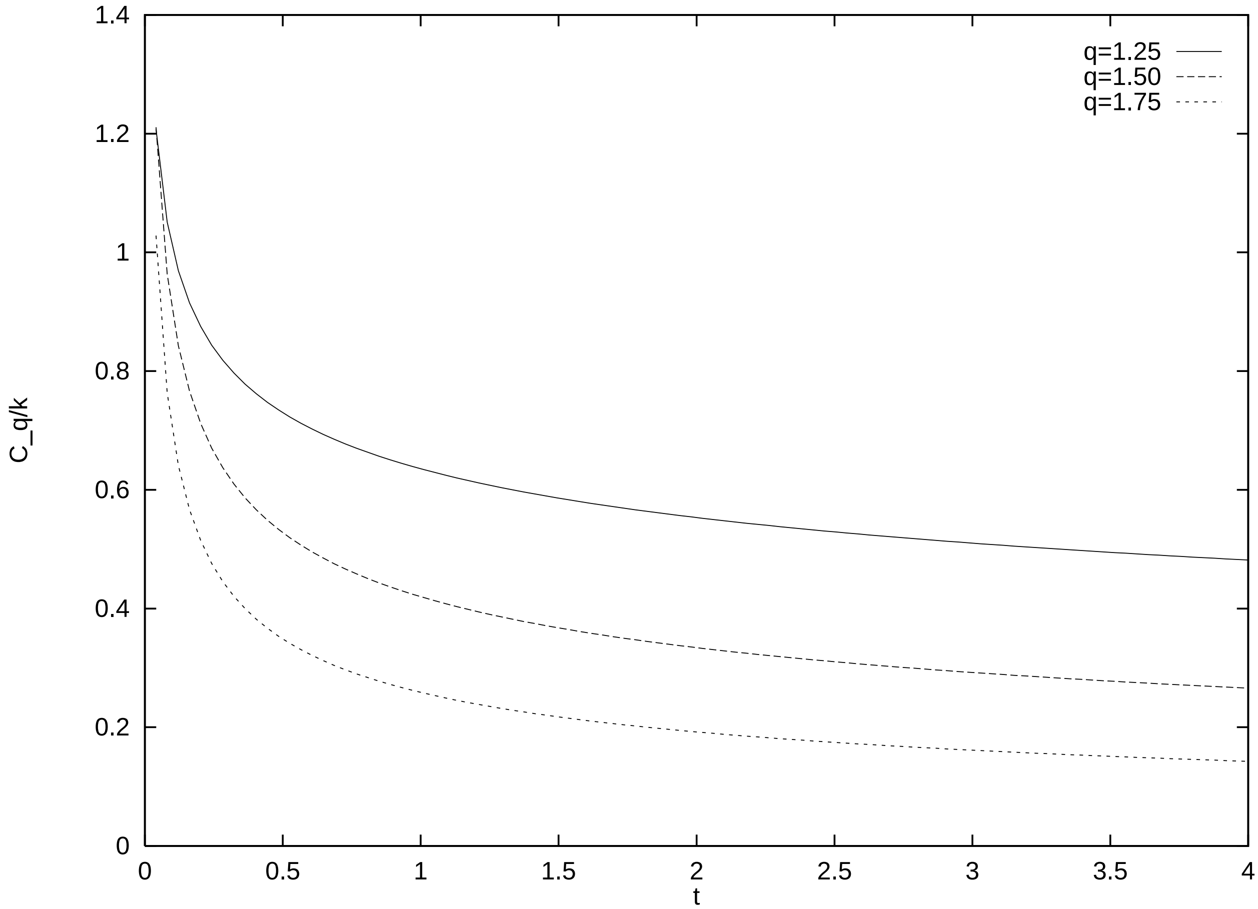

FIG. 2. Specific of the rigid rotator heat as a function of reduced temperature t=T/θ in the low temperature limit.

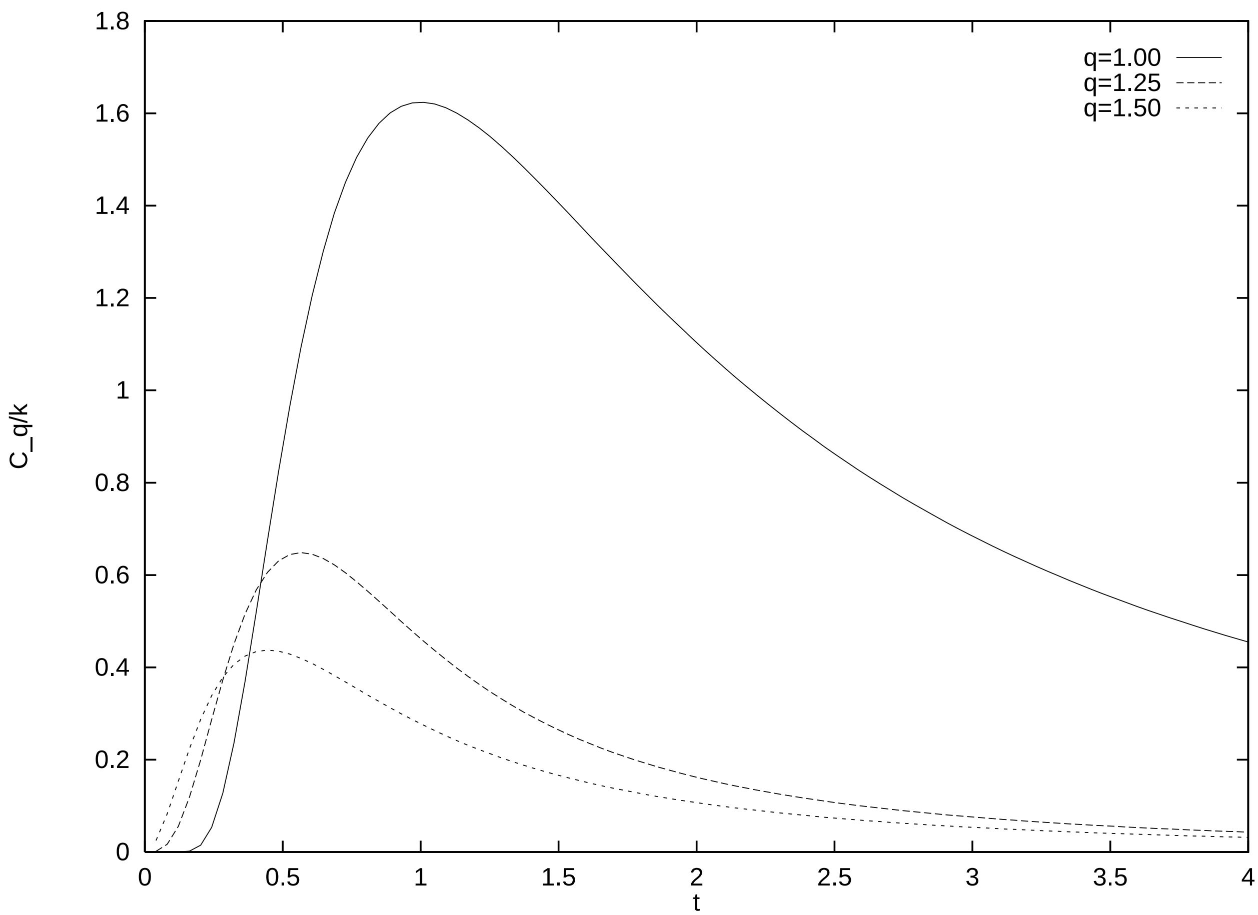

FIG. 3. Specific heat of the non-rigid rotator as a function of temperature in the high temperature limit.

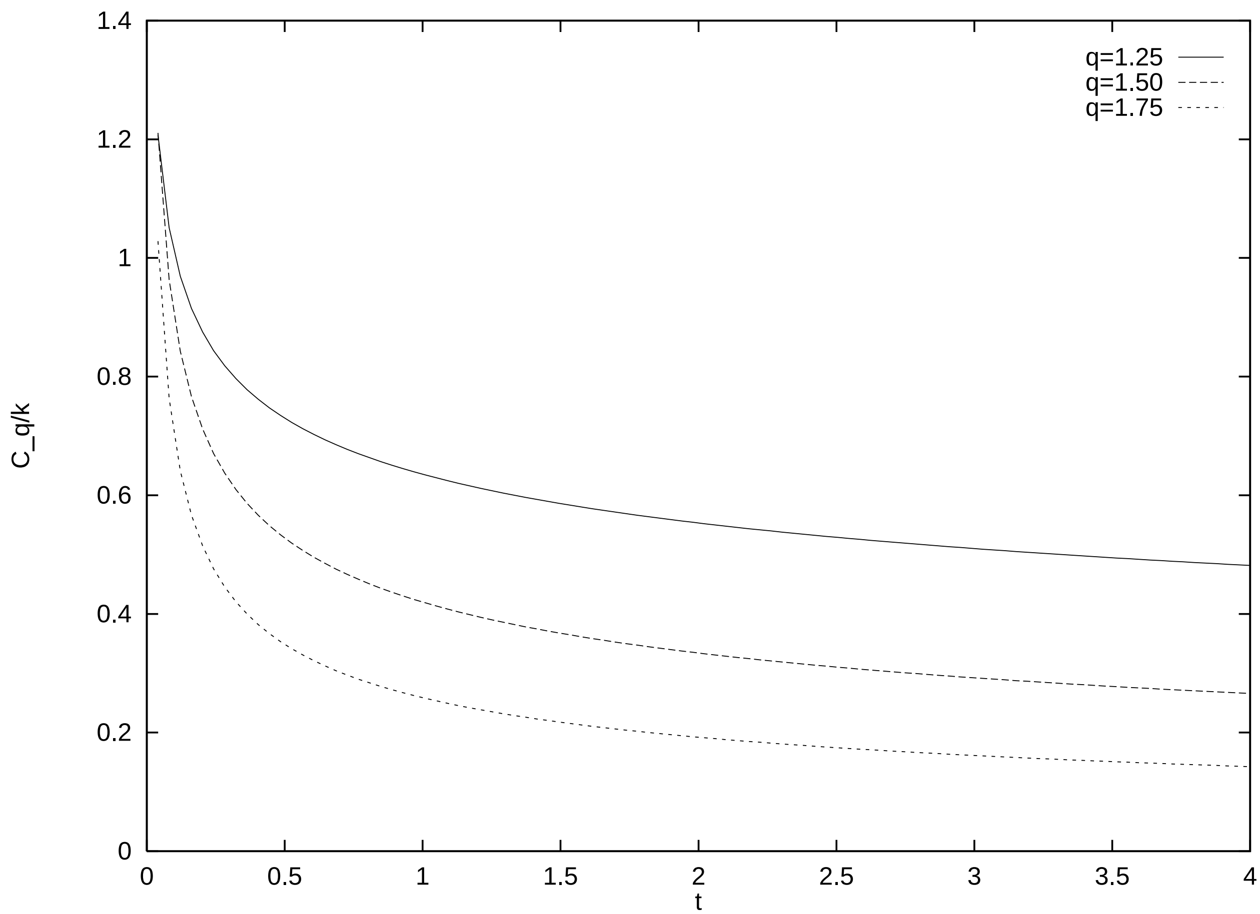

FIG. 4. Specific heat of the non-rigid rotator as a function of temperature in the low temperature limit for q= 1.25, 1.50 and 1.75 respectively starting from above.