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Nonextensive Statistical Mechanics Application to Vibrational Dynamics of Protein Folding

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Abstract The vibrational dynamics of protein folding is analyzed in the framework of Tsallis statistics. We employ exact expressions for classical harmonic oscillators by considering the unnormalized constraints. As $q \to 1$, we show that these approximations agree with the result of Gaussian network model.

Keywords Tsallis statistics · Harmonic oscillator · Protein folding · Temperature factor

1 Introduction

In spite of its great success, the statistical mechanics paradigm based on Boltzmann–Gibbs entropy seems to be unable to deal with many interesting physical scenarios [1]. In 1988 Tsallis advanced a nonextensive generalization of Boltzamann–Gibbs entropic measure. From the year 1988 up to the present days, numerous concepts of the statistical mechanics and thermodynamics have been tackled in the frame of this generalization. Amongst them, the specific heat of the harmonic oscillator [2], one-dimensional Ising model [3, 4], the Boltzmann H-theorem [5–7], the Ehrenfest theorem [8], quantum statistics [9, 10], paramagnetic systems [11], Cercle maps [12], Henon map [13], Haldane exclusion statistics [14] could be enumerated. The generalization which has been successfully nonextensive statistical mechanics is based on the following expression [15]

$$S_q = k\frac{1 - \mathrm{Tr}\,\rho^q}{q-1}. \tag{1}$$

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In the Tsallis statistics, the nonextensive canonical distribution is given by

$$\rho_q = \frac{1}{Z_q}[1-(1-q)\beta H]^{1/(1-q)}, \tag{2}$$

where

$$Z_q = \int \prod_{n=1}^{N} dp_n dx_n [1-(1-q)\beta H]^{1/(1-q)} \tag{3}$$

is the partition function with $q \in \mathbf{R}$ and $\beta \equiv 1/T$ (with $k=1$). Equation (2) is obtained maximizing the Tsallis entropy [15, 16], (1), subject to the constraints

$$U_q = \int \prod_{n=1}^{N} \mathrm{d}p_n \mathrm{d}x_n \rho^q H \tag{4}$$

and

$$\int \prod_{n=1}^{N} \mathrm{d}p_n \mathrm{d}x_n \rho^q = 1, \tag{5}$$

with U_q being the generalized internal energy. In this context, it is employed

$$A_q = \langle A \rangle_q = \int \prod_{n=1}^{N} \mathrm{d}p_n \mathrm{d}x_n \rho^q A \tag{6}$$

as the generalized mean value of the classical function $A(p,x)$ and thermodynamical functions like free energy and specific heat are defined as $F_q = (Z_q^{q-1}-1)/[(1-q)\beta]$, and $C_q = \partial U_q/\partial T$.

We focus our discussion on the classical Tsallis statistics by considering protein folding and harmonic approximation *i.e.*, we employ the Hamiltonian

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{\gamma}{2} \Delta R_i^T L \Delta R_i \tag{7}$$

where the first term is the kinetic energy of the system, γ being the strength of the springs that are assumed as homogeneous, R_i and ΔR_i indicating the equilibrium position and the displacement with respect to R_i of the i-th C_α atoms. The model is eventually defined by the contact matrix L with entries: $L_{ij} = 1$ if the distance $|\mathbf{R}_i - \mathbf{R}_j|$ between two C_α's, in the native conformation, is below the cutoff R_0, while is 0 otherwise. From (3), partition function for the Gaussian Network model [18] which has above Hamiltonian is given by

$$Z_q = \int \prod_{i=1}^{N} \mathrm{d}p_i \mathrm{d}\Delta R_i \left[1-(1-q)\beta\left(\sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{\gamma}{2}\Delta R_i^T L \Delta R_i\right)\right]^{1/(1-q)} \tag{8}$$

we introduce the variables $L = V^T \lambda V$, $x = V\Delta R$ and thus $\Delta R^T L \Delta R = x^T \lambda x$ if λ is eigenvalues of the L and V is eigenvectors of L. We can rewrite partition function as:

$$Z_q = \int \prod_{i=1}^{N} \mathrm{d}p_i \mathrm{d}x_i \left[1-(1-q)\beta\left(\sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{\gamma}{2}\lambda_i x_i^2\right)\right]^{1/(1-q)}. \tag{9}$$

To calculate this integral we introduce the variables: $y_i = [(1-q)\gamma\lambda i\beta/2]^{1/2}x_i$ and $y_{N+i} = [(1-q)\beta/(2m)]^{1/2}p_i$ [17], where $i = 1, 2, 3, \ldots, N$. In terms of these variables, Z_q becomes

$$Z_q = \left\{\prod_i^N \left[\frac{2}{(1-q)\lambda_i\beta}\left(\frac{m}{\gamma}\right)^{1/2}\right]\right\}\int\prod_{n=1}^{2N}\mathrm{d}y_n\left(1-\sum_{k=1}^{2N}y_k^2\right)^{1/(1-q)}. \tag{10}$$

By using hyperspherical coordinates with $u = (\sum_{n=1}^{2N} y_n^2)^{1/2}$ and performing the integral over the angular variables, we obtain

$$Z_q = \left\{\prod_{n=1}^N \left[\frac{2}{(1-q)\lambda_n\beta}\left(\frac{m}{\gamma}\right)^{1/2}\right]\right\}\frac{\Omega_{2N}}{2}\int_0^1 \mathrm{d}u u^{N-1}(1-u)^{1/(1-q)}. \tag{11}$$

By substituting the expression for the solid angle [19] $\Omega_{2N} = 2\pi^N/\Gamma(N)$, and employing integral representation of Euler beta function [20], we verify that

$$\begin{aligned} Z_q &= \left\{\prod_{n=1}^N \left[\frac{2\pi}{(1-q)\lambda_n\beta}\left(\frac{m}{\gamma}\right)^{1/2}\right]\right\}\frac{\Gamma(\frac{1}{1-q}+1)}{\Gamma(\frac{1}{1-q}+1+N)} \\ &= \left[\left(\frac{2-q}{1-q}\right)_N\right]^{-1}\prod_{n=1}^N\left[\frac{2\pi}{(1-q)\lambda_n\beta}\left(\frac{m}{\gamma}\right)^{1/2}\right], \end{aligned} \tag{12}$$

where $(a)_n = a(a+1)(a+2)\cdots(a+n-1) = \frac{(a+n-1)!}{(a-1)!}$ is the Pochhammer symbol [20]. Free energy of the system is given by

$$F_q = -\frac{1}{\beta}\ln_q Z_q \tag{13}$$

and

$$F_q = -\frac{1}{\beta}\ln_q\left[\left(\frac{2-q}{1-q}\right)_N\right]^{-1}\prod_{n=1}^N\left[\frac{2\pi}{(1-q)\lambda_n\beta}\left(\frac{m}{\gamma}\right)^{1/2}\right] \tag{14}$$

and then

$$F_q = -\frac{1}{\beta}\ln_q\left[\left(\frac{2-q}{1-q}\right)_N\right]^{-1}\left[\frac{2\pi}{(1-q)\beta}\left(\frac{m}{\gamma}\right)^{1/2}\right]^N(\det(L^{-1}))^{1/2}. \tag{15}$$

The generalized internal energy can be calculated from the identity $U_q = F_q - T\partial F_q/\partial T$, so it is given by

$$U_q = \frac{N}{\beta}Z_q^{1-q}\frac{N}{\beta}\left\{\left[\frac{2\pi}{(1-q)\beta}\left(\frac{m}{\gamma}\right)^{1/2}\right]^N(\det(L^{-1}))^{1/2}\left[\left(\frac{2-q}{1-q}\right)_N\right]^{-1}\right\}^{1-q}. \tag{16}$$

Hence, we obtained that thermodynamic properties of the system and then the comparison between experimental data and above results is obtained via the X-ray crystallographic B-factors, measuring the mean square fluctuation of C_α atoms around their native positions

$$B_{iq}(T) = \frac{8\pi^2}{3}\langle x_i x_j\rangle_q \tag{17}$$

with $\langle\cdot\rangle$ indicating the thermal average. Where $\langle x_i x_j\rangle_q$ is defined by

$$\langle x_i x_j\rangle_q = \frac{1}{Z_q^q}\int Dx\,Dp x_i x_j [1-(1-q)\beta H]^{\frac{q}{1-q}} \tag{18}$$

or

$$\langle x_i x_j\rangle_q = \frac{1}{Z_q^q}\int Dx\,Dp x_i x_j \left[1-(1-q)\beta\sum_{i=1}^{N}\frac{p_i^2}{2m}+\frac{\gamma}{2}\lambda_i x_i^2\right]^{\frac{q}{1-q}}. \tag{19}$$

In the GGNM (generalized Gaussian network model) approximation, this average is easily carried out, because amounts to a non-Gaussian integration, and B-factors can be expressed in terms of the diagonal part of the inverse of the matrix

$$\langle x_i \cdot x_j\rangle_q = \frac{3k_B T}{\gamma}\left[\frac{L_{ij}^{-1}}{1+(1-q)(N+1)}\right]. \tag{20}$$

Substituting (20) into (17) gives

$$B_{iq}(T) = \frac{8\pi^2 k_B T}{\gamma}\left[\frac{L_{ij}^{-1}}{1+(1-q)(N+1)}\right]. \tag{21}$$

If $q \to 1$, it is calculated that same result of the Gaussian network model as

$$B_i(T) = \frac{8\pi^2 k_B T}{\gamma}[L_{ij}^{-1}]. \tag{22}$$

2 Conclusion

In this study, we obtained that temperature factor or Beta factor using by Tsallis statistical mechanics. In this framework, by the approximate scheme which we have used here, closed and analytical expressions for the generalized Gaussian network model have been derived for harmonic oscillator. In addition to this, the beta factor is q dependent. Since the Beta factor must be positive, q ≤ 1. This show that q must be less or equal unity for harmonic oscillator system. In the $q \to 1$ case, it is observed that, both of the two expressions transforms to the results obtained in the standard Boltzmann–Gibbs statistics.

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