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Exploiting Tsallis Statistics

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Abstract. Two incarnations of the canonical ensemble probability distribution based on the generalization of statistical mechanics of Tsallis are described. A generalization of the law of mass action is used to derive equilibrium constants. Reaction rate constants for barrier crossing are derived using the transition state theory approximation. Monte Carlo and Molecular Dynamics algorithms which can be used to sample Tsallis statistical distributions are defined. The results are used to demonstrate that MC and MD algorithms which sample the Tsallis statistical distributions can be expected to enhance the rate of phase space sampling in simulations of many body systems.

1 An Introduction to Tsallis Statistics

Nearly ten years ago, Tsallis proposed a possible generalization of Gibbs-Boltzmann statistical mechanics.[1] He built his intriguing theory on a re-expression of the Gibbs-Shannon entropy $S = -k \int p(\Gamma) \ln p(\Gamma) d\Gamma$ written

$$S = \lim_{q \rightarrow 1} S_q = \lim_{q \rightarrow 1} \frac{k}{q-1} \int p_q(\Gamma) (1 - [p_q(\Gamma)]^{q-1}) d\Gamma \quad (1)$$

where $d\Gamma = d\mathbf{r}^N d\mathbf{p}^N$ is a phase space increment. On the right, the “replica trick” identity $\ln x = \lim_{n \rightarrow 0} (x^n - 1)/n$ has been used; q is a real number.[1, 2]

Tsallis studied the properties of S_q which he referred to as a “generalized entropy.” He noted that much of the standard mathematical structure of Gibbs-Boltzmann statistical mechanics remained intact *before* the limit is taken; that is, for $S_{q \neq 1}$. This prompted the use of a generalized formalism based on the non-additive entropy S_q to re-derive, for non-extensive systems, a variety of results of the standard statistical mechanics (see [3] and references therein). For example, it is possible to define the probability of finding the system at a given point in phase space $\Gamma = (\mathbf{r}^N, \mathbf{p}^N)$ by extremizing S_q subject to the constraints

$$\int p_q(\Gamma) d\Gamma = 1 \quad \text{and} \quad \int [p_q(\Gamma)]^q H(\Gamma) d\Gamma = E_q \quad (2)$$

where $H(\Gamma)$ is the system Hamiltonian for N distinguishable particles in d dimensions. The result is

$$p_q(\Gamma) = \frac{1}{Z_q h^{dN}} [1 - (1 - q)\beta H(\Gamma)]^{\frac{1}{1-q}} \quad (3)$$

where

$$Z_q = \frac{1}{h^{dN}} \int [1 - (1 - q)\beta H(\Gamma)]^{\frac{1}{1-q}} d\Gamma \quad (4)$$

plays the role of the canonical ensemble partition function. Using the identity $\lim_{n \rightarrow 0} (1 + an)^{1/n} = \exp(a)$, in the limit that $q = 1$, the standard probability of classical Gibbs-Boltzmann statistical mechanics

$$p(\Gamma) = \frac{1}{Z h^{dN}} \exp(-\beta H(\Gamma)) \quad (5)$$

is recovered.

1.1 Surely You're Joking, Mr. Tsallis

Before the limit is taken, the properties of the probability distribution appear to be strange in at least five ways.

(1) In the $q \neq 1$ regime, for certain points in phase space the probability $p_q(\Gamma)$ may be negative or even imaginary. We then say that the probability of the system accessing that point in phase space is zero. This may be the case even when the energy is finite.

(2) Equally foreign is the property that when $q \neq 1$ the relative probability of two points in phase space depends on the choice of the zero of energy.[1] By defining

$$\bar{H}(\Gamma) = \frac{1}{\beta(q-1)} \ln [1 - (1 - q)\beta H(\Gamma)] \quad (6)$$

the probability of being at a point Γ in phase space can be written in the familiar form

$$p(\Gamma) = \frac{1}{Z h^{dN}} \exp(-\beta \bar{H}(\Gamma)) \quad (7)$$

However, for a constant potential shift ϵ the relative probability

$$\frac{p_q(\Gamma_{\text{new}})}{p_q(\Gamma_{\text{old}})} = \left[\frac{1 - (1 - q)\beta(H(\Gamma_{\text{new}}) + \epsilon)}{1 - (1 - q)\beta(H(\Gamma_{\text{old}}) + \epsilon)} \right]^{\frac{1}{1-q}} \quad (8)$$

depends on ϵ . This ratio can be rewritten as

$$\frac{p_q(\Gamma_{\text{new}})}{p_q(\Gamma_{\text{old}})} = \left[\frac{1 - (1 - q)\beta' H(\Gamma_{\text{new}})}{1 - (1 - q)\beta' H(\Gamma_{\text{old}})} \right]^{\frac{1}{1-q}} \quad (9)$$

where potential shift ϵ has been absorbed in an effective “temperature”

$$\frac{1}{\beta'} = \frac{1}{\beta} + (q - 1)\epsilon. \quad (10)$$

In the $q = 1$ limit, the effective temperature equals the standard temperature. Otherwise, adding a constant shift to the potential energy is equivalent to rescaling the temperature at which the canonical probability distribution is computed.

(3) Equilibrium average properties are calculated using a statistical weighting of the probability $p_q(\Gamma)$ of Eq. (3) raised to the power of q as required by the generalized statistical mechanics. The so-called q -expectation value is written

$$\langle \dots \rangle_q = \int [p_q(\Gamma)]^q \dots d\Gamma. \quad (11)$$

In general, $\langle 1 \rangle_q \neq 1$ for $q \neq 1$. Clearly, this is an odd “average!” It is also inconvenient as it requires evaluation of Z_q .

(4) Is the “temperature” $1/\beta$ related to the variance of the momentum distribution as in the classical equipartition theorem? It happens that there is no simple generalization of the equipartition theorem of classical statistical mechanics. For the $2N$ dimensional phase space $\Gamma = (x_1 \dots x_N, p_1, \dots p_N)$ the ensemble average for a *harmonic* system is

$$\frac{\langle p_k^2 \rangle_q}{\langle 1 \rangle_q} = \frac{\int [p_q(\Gamma)]^q p_k^2 d\Gamma}{\int [p_q(\Gamma)]^q d\Gamma} = \frac{1}{\beta} \frac{1}{1 - (q-1)N} \quad (12)$$

where we assume unit mass. For the case of $q = 1$ we find the standard result that $\langle p_k^2 \rangle = 1/\beta$. In general we find that the average is proportional to $1/\beta$ but not equal to it. The situation is equally strange for the unnormalized “multifractal” average where

$$\langle p_k^2 \rangle_q = \text{stuff} \times \frac{1}{\beta^{1+(1-q)N/2}} \quad (13)$$

but the “stuff” is a q -dependent constant that may be negative or imaginary!

The distribution of momenta cannot be written as a product of single particle distributions and we find that

$$\langle p_k^2 + p_k^2 \rangle_q \neq 2 \langle p_k^2 \rangle_q. \quad (14)$$

There is no simple linear scaling of the variance of the momentum with the number of degrees of freedom.

(5) When $q = 1$ the extensivity of the entropy can be used to derive the Boltzmann entropy equation $S = k \ln W$ in the microcanonical ensemble. When $q \neq 1$, it is the odd property that the generalization of the entropy S_q is not extensive that leads to the peculiar form of the probability distribution. The non-extensivity of S_q has led to speculation that Tsallis statistics may be applicable to gravitational systems where interaction length scales comparable to the system size violate the assumptions underlying Gibbs-Boltzmann statistics.[4]

1.2 Ideal Systems

Let's focus on the $q > 1$ regime for systems with a Hamiltonian of the form

$$H(\Gamma) = \sum_k^N \frac{1}{2m} \mathbf{p}_k^2 + U(\mathbf{r}^N), \quad (15)$$

in d -dimensional space, the partition function can be written as

$$Z_q = \left(\frac{1}{\Lambda \sqrt{q-1}} \right)^{dN} \frac{\Gamma(\frac{1}{q-1} - \frac{dN}{2})}{\Gamma(\frac{1}{q-1})} \int [1 - (1-q)\beta U(\mathbf{r}^N)]^{\frac{1}{1-q} + \frac{dN}{2}} d\mathbf{r}^N \quad (16)$$

where $\Lambda = \sqrt{\hbar^2 \beta / 2\pi m}$ is the thermal de Broglie wavelength of the k th oscillator. For an ideal gas of N particles where $U = 0$ we find

$$Z_q = \left(\frac{L}{\Lambda \sqrt{q-1}} \right)^{dN} \frac{\Gamma(\frac{1}{q-1} - \frac{dN}{2})}{\Gamma(\frac{1}{q-1})} \quad (17)$$

where L is the length of a side of a cubic box containing the ideal gas. In the limit that $q \rightarrow 1$ we can use the asymptotic approximation $\Gamma(x+a)/\Gamma(x+b) = x^{a-b}$, good for large x , to show that the standard partition function for an ideal gas is recovered

$$\lim_{q \rightarrow 1} Z_q = \left(\frac{L}{\Lambda} \right)^{dN}. \quad (18)$$

Now consider a system of N one-dimensional harmonic oscillators with the Hamiltonian

$$H(\Gamma) = \sum_k^N \left[\frac{1}{2m} p_k^2 + \frac{1}{2} m \omega_k^2 x_k^2 \right]. \quad (19)$$

The canonical ensemble partition function is the phase space integral

$$Z_q = \frac{1}{h^N} \int dx^N \int dp^N [1 - (1-q)\beta H(\Gamma)]^{\frac{1}{1-q}}. \quad (20)$$

The configuration integral can be evaluated and the partition function is

$$Z_q = \left(\frac{2\pi}{h\beta(q-1)} \right)^N \frac{\Gamma(\frac{1}{q-1} - N)}{\Gamma(\frac{1}{q-1})} \prod_k^N \frac{1}{\omega_k} \quad (21)$$

Note that there is not a unique separation of the partition function as $Z_q = Z_q^{\text{trans}} Z_q^{\text{vib}}$. However, using the result for the ideal gas translational partition function

$$Z_q^{\text{vib}} = \left(\frac{2\pi}{m\beta(q-1)} \right)^{N/2} \frac{1}{L^N} \frac{\Gamma(\frac{1}{q-1} - N)}{\Gamma(\frac{1}{q-1} - \frac{N}{2})} \prod_k^N \frac{1}{\omega_k} \quad (22)$$

In the limit that $q \rightarrow 1$ we see that

$$\lim_{q \rightarrow 1} Z_q = \left(\frac{2\pi}{\beta h} \right)^N \prod_k \frac{1}{\omega_k} \quad (23)$$

and the canonical ensemble partition function for N harmonic oscillators in classical Gibbs-Boltzmann statistics is recovered.

1.3 Ensemble Averages and the “ q -Expectation Value”

For certain values of q and a harmonic potential, the distribution $p_q(\Gamma)$ can have infinite variance and higher moments. This fact has motivated the use of the q -expectation value to compute the average of an observable A

$$\langle A \rangle_q = \frac{1}{(Z_q h^N)^q} \int A(\Gamma) [1 - (1 - q)\beta H(\Gamma)]^{\frac{q}{1-q}} d\Gamma. \quad (24)$$

Since the averaging operator is not normalized and in general $\langle 1 \rangle_q \neq 1$ for $q \neq 1$, it is necessary to compute Z_q to determine the average. To avoid this difficulty, we employ a different generalization of the canonical ensemble average

$$\langle A \rangle_q = \frac{\int A(\Gamma) [1 - (1 - q)\beta H(\Gamma)]^{\frac{q}{1-q}} d\Gamma}{\int [1 - (1 - q)\beta H(\Gamma)]^{\frac{q}{1-q}} d\Gamma}, \quad (25)$$

which is obviously normalized.

Consider a system of N particles in d dimensions. Using the standard procedure of integrating over the momenta in Cartesian coordinates, we can write the average of a mechanical property $A(\mathbf{r}^N)$ as

$$\langle A \rangle_q = \frac{\int A(\mathbf{r}^N) [1 - (1 - q)\beta U(\mathbf{r}^N)]^{\frac{q}{1-q} + \frac{dN}{2}} d\mathbf{r}^N}{\int [1 - (1 - q)\beta U(\mathbf{r}^N)]^{\frac{q}{1-q} + \frac{dN}{2}} d\mathbf{r}^N} \quad (26)$$

This definition is based on and proportional to the q -expectation value. However, it is more useful since it is not necessary to evaluate the partition function to compute an average.

1.4 Monte Carlo Methods for Pure Tsallis Statistics

A configurational Monte Carlo algorithm based on uniform random trial moves and the acceptance probability

$$p = \min \left[1, \left(\frac{p_q(\mathbf{r}_{\text{new}}^N)}{p_q(\mathbf{r}_{\text{old}}^N)} \right)^{q + \frac{dN}{2}(1-q)} \right], \quad (27)$$

where $p_q(\mathbf{r}) \propto [1 - (1 - q)\beta U(\mathbf{r})]^{-\frac{1}{1-q}}$, will sample the configurational distribution dictated by Eq. (26). Such a Monte Carlo algorithm may be used to compute equilibrium averages in the Tsallis statistical distribution.

In the thermodynamic limit of large N for $q \neq 1$ we find that the acceptance probability is unity for even the largest positive change in potential energy ΔU . Effectively, the Monte Carlo sampling reduces to a random walk on the potential energy landscape. This feature can be used to devise a sampling scheme to overcome broken ergodicity. Only part of the time the acceptance would be that in Eq. (27), while the rest of the time will be spent sampling according to the standard Metropolis criterion.

Alternatively, one may use a phase space Monte Carlo method with uniform random trial moves and an acceptance probability

$$p = \min \left[1, \left(\frac{p_q(\Gamma_{\text{new}})}{p_q(\Gamma_{\text{old}})} \right)^q \right] \quad (28)$$

to sample the phase space distribution $[p_q(\Gamma)]^q$. In the thermodynamic limit, this form of the acceptance probability does not suffer from the peculiar behavior exhibited by the form above. Moreover, an algorithm of this sort can be used to calculate standard, Gibbs-Boltzmann ($q = 1$) equilibrium thermodynamic averages

$$\langle A \rangle = \left\langle \frac{A e^{-\beta H(\Gamma)}}{[1 - (1 - q)\beta H(\Gamma)]^{\frac{q}{1-q}}} \right\rangle_q \left\langle \frac{e^{-\beta H(\Gamma)}}{[1 - (1 - q)\beta H(\Gamma)]^{\frac{q}{1-q}}} \right\rangle_q^{-1}. \quad (29)$$

Using this expression, the standard $q = 1$ equilibrium average properties may be calculated over a trajectory which samples the generalized statistical distribution for $q \neq 1$ with the advantage of enhanced sampling for $q > 1$.

1.5 Chemical Equilibrium

Consider the chemical equilibrium



The general form of the equilibrium constant is

$$K_{eq} = \frac{X_\gamma}{X_\alpha} = \frac{\int [p_q]^q \theta_\gamma(\Gamma) d\Gamma}{\int [p_q]^q \theta_\alpha(\Gamma) d\Gamma} \quad (31)$$

where X_α and X_γ are mole fractions of reactants and products, and the Heaviside functions $\theta_\alpha(\Gamma)$ and $\theta_\gamma(\Gamma)$ are unity for phase space points in well α and γ , respectively, and zero otherwise. We will restrict our evaluation to one dimension; extension to many dimensions is straightforward.

In the limit that the barrier height is large compared with the thermal energy, it is standard practice to expand the potential near the reactant well

minimum to quadratic order and approximate the integral by the contribution near the well minimum. This approximation is well justified when the thermal distribution is Gaussian and relatively short-ranged. However, for $q > 1$ the approximation is not so easily justified. For $q = 2$ the equilibrium distribution for a harmonic well is a Cauchy-Lorentz distribution so that it is likely that significant contributions from anharmonicity far from the well minimum will contribute to the integral. Aware of this limitation, we carry out the integral using a harmonic approximation to the α and γ potential wells. For the α state well

$$U(x) \simeq U(x_\alpha) + m\omega_\alpha^2(x - x_\alpha)^2/2 \quad (32)$$

We follow this with a low temperature approximation to the integral over the well's phase space population. The resulting equilibrium constant is

$$K_{eq}(\beta; q) = \frac{X_\gamma}{X_\alpha} = \frac{\omega_\alpha}{\omega_\gamma} \left[\frac{1 - (1 - q)\beta U(x_\alpha)}{1 - (1 - q)\beta U(x_\gamma)} \right]^{\frac{1}{1-q}}. \quad (33)$$

In the limit that $q \rightarrow 1$, the equilibrium distributions are more delocalized and the low temperature approximation may not be well justified.

1.6 Transition State Theory for Rates of Barrier Crossing

The transition state theory estimate of the rate constant for barrier crossing provides an upper bound on the rate of transition between well-defined reactant and product states. An assumption of the theory is that once a reactant acquires enough energy to cross the barrier, it will cross the transition state and be deactivated as product. Dynamical recrossings of the transition state, associated with weak or strong damping, or nonadiabatic transitions, lead to reductions in the rate of barrier crossing from the transition state theory estimate. In this section, we examine the transition state theory rate constant for Tsallis statistics. This discussion is restricted to one-dimension, but the generalization to many dimensions is straightforward.

There is still some debate regarding the form of a dynamical equation for the time evolution of the density distribution in the $q \neq 1$ regime. Fortunately, to evaluate the rate constant in the transition state theory approximation, we need only know the form of the equilibrium distribution. It is only when we wish to obtain a more accurate estimate of the rate constant, including an estimate of the transmission coefficient, that we need to define the system's dynamics.

For a one-dimensional bistable potential with the transition state positioned along the reaction coordinate x at $x = x^\ddagger$, the TST rate for forward reaction is defined as

$$k_{TST}(\beta; q) = \frac{\int \delta(x - x^\ddagger) v \Theta(v) [p_q(\Gamma)]^q d\Gamma}{\int \Theta(x^\ddagger - x) [p_q(\Gamma)]^q d\Gamma} \quad (34)$$

where $p_q(\Gamma) = p_q(x, v)$ is the generalized statistical distribution

$$p_q(x, v) = \frac{1}{Z_q h} [1 - (1 - q)\beta H(x, v)]^{\frac{1}{1-q}} \quad (35)$$

where

$$Z_q = \frac{1}{h} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dv [1 - (1 - q)\beta H(x, v)]^{\frac{1}{1-q}} \quad (36)$$

is the generalized partition function and $H(x, v) = mv^2/2 + U(x)$ is the Hamiltonian.

For $q < 1$ there can be difficulties which arise from distributions which have zero probability in the barrier region and zero rate constant. In our analysis we assume that for any q the zero of energy is chosen such that the probability $p_q(\Gamma)$ is positive and real for all Γ . The transition state theory rate constant as a function of the temperature and q is

$$k_{TST}(\beta; q) = \frac{\Gamma(\frac{q}{q-1})}{\Gamma(\frac{q}{q-1} - \frac{1}{2})} \left(\frac{q-1}{2\pi m\beta} \right)^{1/2} [1 - (1 - q)\beta U(x^\ddagger)]^{\frac{1}{1-q}} \frac{1}{\chi(\beta; q)} \quad (37)$$

where

$$\chi(\beta; q) = \int_{-\infty}^{x^\ddagger} [1 - \beta(1 - q)U(x)]^{\frac{q}{1-q} + \frac{1}{2}} dx. \quad (38)$$

We can approximate this fraction of states in the reactant well, by expanding the potential in a harmonic approximation and assuming that the temperature is low compared with the barrier height. This leads to an estimate for the rate constant

$$k_{TST}(\beta; q) = \frac{\omega_\alpha}{2\pi} \left[\frac{1 - (1 - q)\beta U(x^\ddagger)}{1 - (1 - q)\beta U(x_\alpha)} \right]^{\frac{1}{1-q}}. \quad (39)$$

As we expect, in the limit that $q \rightarrow 1$ the standard transition state theory result

$$k_{TST}(\beta; q = 1) = \frac{\omega_\alpha}{2\pi} \exp[-\beta(U(x^\ddagger) - U(x_\alpha))] \quad (40)$$

is recovered.

Returning to the more general expression, in the low temperature limit we find that the rate

$$k_{TST}(\beta; q) \rightarrow \frac{\omega_\alpha}{2\pi} \left[\frac{U(x^\ddagger)}{U(x_\alpha)} \right]^{\frac{1}{1-q}} \quad (41)$$

independent of the temperature (even when $T=0$)! For the special case of $q = 2$ we find

$$k_{TST}(\beta; q = 2) = \frac{\omega_\alpha}{2\pi} \left[\frac{1 + \beta U(x_\alpha)}{1 + \beta U(x^\ddagger)} \right] \quad (42)$$

1.7 Temperature Scaling in Simulated Annealing

Using these results, we can derive a scaling relation for the optimal cooling schedule in a simulated annealing optimization protocol. We suppose that the relevant energy scales of $U(\mathbf{r}^N)$ are bounded by ΔU , the difference in energy between the ground and first excited state minima, and U^\ddagger , the highest barrier on the potential surface accessed from the global energy minimum. The final temperature (maximum β) reached in a simulated annealing run must be small enough so that at equilibrium the mole fraction in the global energy minimum basin is significant. In other words, based on Eq. (33) we demand that $K_{eq}^{\max} = K_{eq}(\beta_{\max}; q)$.

The time that the trajectory must spend at β_{\max} to ensure that the equilibrium distribution is sampled is at least τ_{\min} , the time required to surmount the largest barrier separating the global energy minimum from other thermodynamically important states. Using Eq. (39) we find

$$\tau_{\min} = \frac{2\pi}{\omega_\alpha} \left[1 - \left(1 - \frac{1}{\eta}\right) \frac{U^\ddagger}{\Delta U} \right]^{\frac{1}{1-q}}. \quad (43)$$

where

$$\eta = \left(\frac{\omega_\alpha}{\omega_\gamma} K_{eq}^{\max} \right)^{q-1}. \quad (44)$$

K_{eq}^{\max} is the maximum allowable equilibrium constant for the ground and first excited state populations at the final and lowest temperature reached in the annealing run, β_{\max} . For most cases of interest, we expect that $\eta \ll 1$.

In the limit $q \rightarrow 1$ of Gibbs-Boltzmann statistics, using the fact that $\lim_{x \rightarrow 0} [1 - a(1 - b^x)]^{1/x} = b^a$, we find that

$$\tau_{\min} = \left(\frac{2\pi}{\omega_\alpha} \right) \eta^{-\frac{U^\ddagger}{\Delta U}}. \quad (45)$$

The time for classical simulated annealing increases exponentially as a function of the ratio of the energy scales $U^\ddagger/\Delta U$. However, for $q > 1$ the situation is qualitatively different. As a result of the weak temperature dependence in the barrier crossing times, the time for simulated annealing increases only weakly as a power law.

2 Maxwell-Tsallis Statistics

We have developed Monte Carlo algorithms based on sampling Tsallisian distributions. Using a uniform random trial move and the acceptance probability

$$p = \min \left[1, \left(\frac{p_q(\mathbf{r}_{\text{new}}^N)}{p_q(\mathbf{r}_{\text{old}}^N)} \right)^q \right]. \quad (46)$$

the detailed balance condition

$$[p_q(x)]^q W(x \rightarrow x') = [p_q(x')]^q W(x' \rightarrow x) \quad (47)$$

is satisfied where $W(x, x')$ is an element of the transition matrix. The walk generated by Eq. (28) will sample the distribution

$$[p_q(\mathbf{r}^N)]^q = \frac{1}{Z_q} [1 - (1 - q)\beta U(\mathbf{r}^N)]^{\frac{q}{1-q}} \quad (48)$$

This probability distribution can be found by extremizing the generalization of the entropy Eq. (1) subject to the constraints

$$\int p_q(\mathbf{r}^N) d\mathbf{r}^N = 1 \quad \text{and} \quad \int [p_q(\mathbf{r}^N)]^q U(\mathbf{r}^N) d\mathbf{r}^N = U_q \quad (49)$$

We might then assume a Maxwell distribution of momenta so that the overall phase space distribution is that of a Maxwell-Tsallis statistics.

2.1 Hybrid Monte Carlo Algorithm

We have implemented the generalized Monte Carlo algorithm using a hybrid MD/MC method composed of the following steps.

1. Velocities are randomly chosen from a Maxwell distribution at a given temperature.
2. The positions and velocities are updated for a time step Δt according to Newton's equation of motion using the force deriving from \bar{U} .
3. The point (phase space point or configuration) is accepted or rejected according to the criterion

$$p = \min [1, \exp[-\beta(\Delta K + \Delta \bar{U})]] \quad (50)$$

where ΔK is the change in standard classical kinetic energy and $\Delta \bar{U}$ is the change in the effective potential energy

$$\bar{U}(\mathbf{r}^N) = \frac{1}{\beta(q-1)} \ln [1 - (1 - q)\beta U(\mathbf{r}^N)]. \quad (51)$$

4. Return to 1.

When the integrator used is reversible and symplectic (preserves the phase space volume) the acceptance probability will exactly satisfy detailed balance and the walk will sample the equilibrium distribution $[p_q(\mathbf{r}^N)]^q$.

A similar algorithm has been used to sample the equilibrium distribution $[p_q(\mathbf{r}^N)]^q$ in the conformational optimization of a tetrapeptide[5] and atomic clusters at low temperature.[6] It was found that when $q > 1$ the search of conformational space was greatly enhanced over standard Metropolis Monte Carlo methods. In this form, the velocity distribution can be thought to be Maxwellian.

2.2 Molecular Dynamics with an Effective Potential

For a given potential energy function $U(\mathbf{r}^N)$, the corresponding generalized statistical probability distribution which is generated by the Monte Carlo algorithm is proportional to

$$P_q(\mathbf{r}^N) = [1 - (1 - q)\beta U(\mathbf{r}^N)]^{\frac{q}{1-q}}. \quad (52)$$

Consider the generalized distribution $P_q(\mathbf{r}^N)$ to be generated in the Gibbs-Boltzmann canonical ensemble ($q = 1$) by an effective potential $\mathcal{W}_q(\mathbf{r}^N; \beta)$ which is defined

$$P_q(\mathbf{r}^N) = \exp(-\beta \mathcal{W}_q(\mathbf{r}^N; \beta)) \quad (53)$$

such that when $q = 1$, $\mathcal{W}(\mathbf{r}^N; \beta) = U(\mathbf{r}^N)$. For $q \neq 1$, the effective potential will depend on temperature as well as the coordinates.

Given this effective potential, it is possible to define a constant temperature molecular dynamics algorithm such that the trajectory samples the distribution $P_q(\mathbf{r}^N)$. The equation of motion then takes on a simple and suggestive form

$$m_k \frac{d^2 \mathbf{r}_k}{dt^2} = -\nabla_{\mathbf{r}_k} \bar{U} = -\nabla_{\mathbf{r}_k} U(\mathbf{r}^N) q [1 - (1 - q)\beta U(\mathbf{r}^N)]^{-1} \quad (54)$$

for a particle of mass m_k and position \mathbf{r}_k and \bar{U} defined by Eq. (51). It is known that in the canonical ensemble a constant-temperature molecular dynamics algorithm generates samples from the configuration space according to the Boltzmann probability. As a result, the molecular dynamics with the effective potential $\mathcal{W}_q(\mathbf{r}^N; \beta)$ will sample from the $P_q(\mathbf{r}^N)$ distribution.

The effective force derived from the effective potential $\mathcal{W}(\mathbf{r}^N)$ has a number of interesting properties. It is of the form $F_q(\mathbf{r}^N; \beta) = -\nabla_{\mathbf{r}_k} \bar{U} = F_1(\mathbf{r}^N) \alpha_q(\mathbf{r}^N; \beta)$ where $F_1(\mathbf{r}^N)$ is the ‘‘exact’’ force for standard molecular dynamics ($q = 1$) and $\alpha_q(\mathbf{r}^N; \beta)$ is a scaling function which is unity when $q = 1$ but can otherwise have a strong effect on the dynamics.

Assume that the potential is defined to be a positive function. In the regime $q > 1$, the scaling function $\alpha_q(\mathbf{r}^N, \beta)$ is largest near low lying minima of the potential. In barrier regions, where the potential energy is large, the scaling function $\alpha_q(\mathbf{r}^N, \beta)$ is small. It may surprise you that for the function to be well defined, βU must be greater than zero.

Use of the effective potential has the effect of reducing the magnitude of the force in the barrier regions. Therefore, a particle attempting to pass over a potential energy barrier will meet with less resistance when $q > 1$ than when $q = 1$. At equilibrium, this leads to more delocalized probability distributions with an increased probability of sampling barrier regions. This argument demonstrates that when $q > 1$ the generalized molecular dynamics or Monte Carlo trajectories will cross barriers more frequently and explore phase space more efficiently (for a review of recent methods for enhanced phase-space sampling see [7]).

2.3 Rate and Equilibrium Constants

We once again carry out the integral in the low temperature approximation and find

$$k_{TST}(\beta; q) = \frac{\omega_\alpha}{2\pi} \frac{\Gamma(\frac{q}{q-1})}{\Gamma(\frac{q}{q-1} - \frac{1}{2})} \frac{1}{\sqrt{1 - (1-q)\beta U(x_\alpha)}} \left[\frac{1 - (1-q)\beta U(x^\ddagger)}{1 - (1-q)\beta U(x_\alpha)} \right]^{\frac{q-1}{q-1}} \quad (55)$$

Within the same approximation, we estimate that the equilibrium constant is

$$K_{eq}(\beta; q) = \frac{X_\beta}{X_\alpha} = \frac{\omega_\alpha}{\omega_\beta} \left[\frac{1 - (1-q)\beta U(x_\alpha)}{1 - (1-q)\beta U(x_\beta)} \right]^{\frac{1}{1-q} + \frac{1}{2}}. \quad (56)$$

As in the case of pure Tsallis statistics and Eq. (33), in the limit that $q \rightarrow 1$ the standard transition state theory result

$$k_{TST}(\beta; q = 1) = \frac{\omega_\alpha}{2\pi} \exp[-\beta(U(x^\ddagger) - U(x_\alpha))] \quad (57)$$

is recovered.

Returning to the more general expression, in the low temperature limit we find that the transition state theory estimate of the rate is

$$k_{TST}(\beta; q) \rightarrow \frac{\omega_\alpha}{2\pi} \left[\frac{U(x^\ddagger)}{U(x_\alpha)} \right]^{\frac{1}{1-q}} \frac{1}{\sqrt{\beta U(x_\alpha)}} \quad (58)$$

which scales as $1/\sqrt{\beta}$ at low temperatures for all q .

For the special case of $q = 2$ we find

$$k_{TST}(\beta; q = 2) = \frac{\omega_\alpha}{\pi} \left[\frac{1 + \beta U(x_\alpha)}{1 + \beta U(x^\ddagger)} \right]^2 \frac{1}{\sqrt{1 + \beta U(x_\alpha)}} \quad (59)$$

For $q = 1$, the normal transition state theory rate constant is independent of temperature at high temperatures and varies exponentially with temperature in the limit of low temperatures (kT small compared with the barrier height U^\ddagger) as

$$k_{TST} \sim \exp(-\beta U^\ddagger). \quad (60)$$

For $q \neq 1$, at high temperature the rate is independent of temperature $k_{TST} = \omega_\alpha/\pi$ which is a factor of two larger than the result for $q = 1$. At low temperature

$$k_{TST} \sim \beta^{-1/2} \quad (61)$$

independent of q ! As q approaches unity the exponential Arrhenius temperature dependence is recovered. However, for larger values of q the temperature scaling of the rate is a weak inverse power law. At all temperatures, the transition state theory rate constant is significantly larger for $q > 1$ than for $q = 1$.

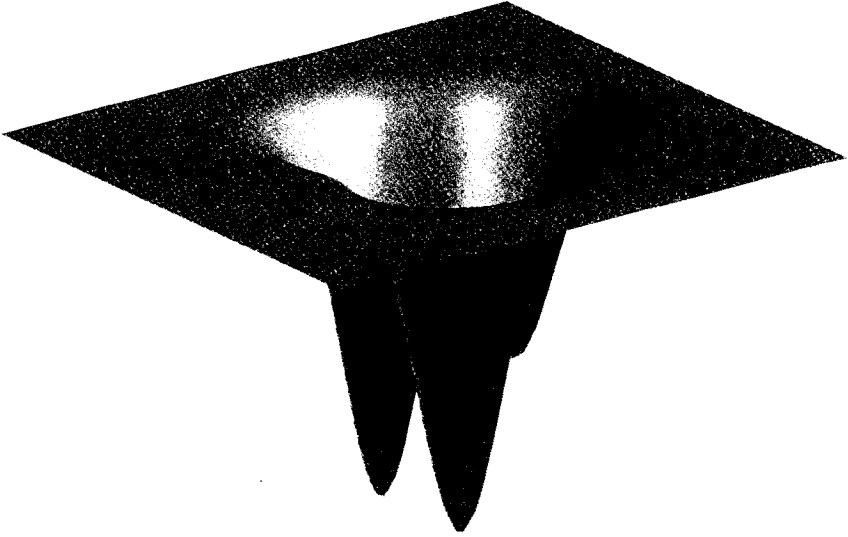


Fig. 1 The two-dimensional potential considered in the text has two deep holes, seen in the front and left sides of the plot, and a less deeper hole to the right.

2.4 Master Equations and Relaxation to Equilibrium

The relaxation of a system to equilibrium can be modeled using a master equation

$$\frac{dP_i}{dt} = \sum_{j \neq i} [L_{ij}P_j(t) - L_{ji}P_i(t)]. \quad (62)$$

The elements of the transition matrix from state j to state i can be estimated in the transition state theory approximation

$$L_{ij} = \frac{\omega_j}{2\pi} \left[\frac{1 + (q-1)\beta U(x_{ij}^\ddagger)}{1 + (q-1)\beta U(x_j)} \right]^{\frac{1}{1-q}}, \quad (63)$$

where the total phase space probability of the j th state is proportional to

$$M_j = \frac{2\pi}{\beta\omega_j} [1 + (q-1)\beta U(x_j)]^{\frac{1}{1-q}}. \quad (64)$$

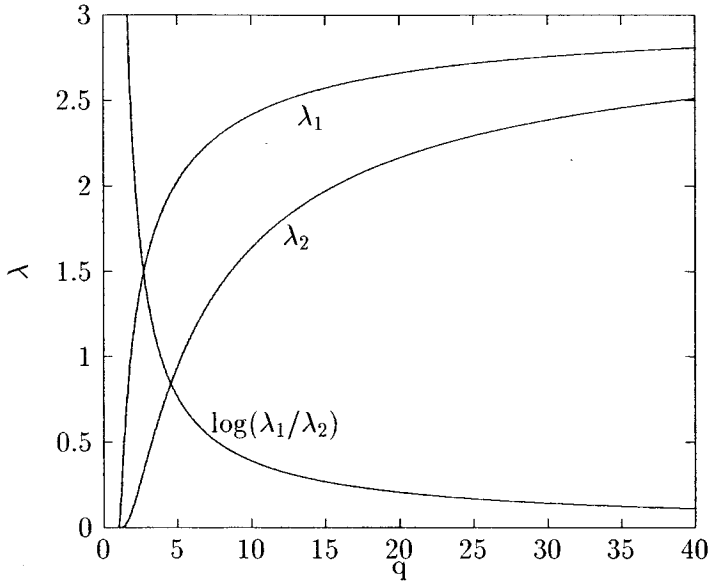


Fig. 2 The dependence on q of the non-zero eigenvalues of the two-dimensional, three-hole model described in the text shows the rapid onset of escape from wells as soon as q exceeds unity and the saturation at higher values of q . Also shown is the logarithm of the ratio of the two non-zero eigenvalues.

The symmetric transmission coefficients are defined $B_{ij} = L_{ij}M_i$. The general solutions are of the form

$$P_i(t) = \sum_n a_n \phi_i^{(n)} \exp(-\lambda_n t) \quad (65)$$

in terms of the eigenfunctions $\phi_i^{(n)}$ and eigenvalues λ_n of the transmission matrix \hat{L} .

We have calculated the eigenvalues for a two-dimensional model system described by a potential function consisting of three holes, two deeper holes of equal depth, and a more shallow hole. The barrier between the deeper holes is higher than the other two barriers, which have equal height.[8] One of the three eigenvalues is zero, for any q , for reasons of conservation of probability. In the figure, we plot the other two as a function of q , together with their ratio. There is to be observed, for a thermal energy of a tenth of the well depth, the quick increase in the magnitude of the eigenvalues for $q > 1$. This implies fast relaxation to equilibrium even at low temperatures, due to the delocalized character of the Tsallisian distributions.

Do we expect this model to be accurate for a dynamics dictated by Tsallis statistics? A jump diffusion process that randomly samples the equilibrium canonical Tsallis distribution has been shown to lead to anomalous diffusion and Lévy flights in the $5/3 < q < 3$ regime.[3] Due to the delocalized nature of the equilibrium distributions, we might find that the microstates of our master equation are not well defined. Even at low temperatures, it may be difficult to identify distinct microstates of the system. The same delocalization can lead to large transition probabilities for states that are not adjacent in configuration space. This would be a violation of the assumptions of the transition state theory - that once the system crosses the transition state from the reactant microstate it will be deactivated and equilibrated in the product state. Concerted transitions between spatially far-separated states may be common. This would lead to a highly connected master equation where each state is connected to a significant fraction of all other microstates of the system.[9, 10]

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