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# SCHOOL and CONFERENCE
# on
# COMPLEX SYSTEMS
# and
# NONEXTENSIVE STATISTICAL MECHANICS

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## Lecture 1: Computer Simulations of Classical Systems Inspired from Tsallis Statistics

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# Lecture 1: Computer Simulations of Classical Systems Inspired from Tsallis Statistics

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# Theoretical Considerations

- Two incarnations of the canonical ensemble based on generalization of statistical mechanics of Tsallis
- A generalization of the law of mass action $\rightarrow$ equilibrium constants. Rate constants for barrier crossing from TST.
- Monte Carlo and Molecular Dynamics algorithms to sample Tsallis statistical distributions. Demonstrate that Tsallis MC and MD algorithms enhance phase space sampling in complex systems. Better optimization methods.

# An introduction to Tsallis statistics

- Generalization of Gibbs-Boltzmann statistical mechanics (Tsallis, 1988). Re-express Gibbs-Shannon entropy $S = -k \int p(\mathbf{\Gamma}) \ln p(\mathbf{\Gamma}) d\mathbf{\Gamma}$ as

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

  where $d\mathbf{\Gamma} = d\mathbf{r}^N d\mathbf{p}^N$ is a phase space increment.

- Inspired by "replica trick" identity $\ln x = \lim_{n \to 0}(x^n - 1)/n$
- Tsallis studied properties of $S_q$, "generalized entropy." Structure of Gibbs-Boltzmann statistics remained intact *before* the limit is taken; that is, for $S_{q \neq 1}$.
- This prompted use of generalized formalism (based on the **non-additive** entropy $S_q$) to re-derive stat mech for non-extensive systems (Tsallis, 1995).
- For example, define probability to be at $\mathbf{\Gamma} = (\mathbf{r}^N, \mathbf{p}^N)$ by

extremizing $S_q$ subject to constraints:

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

where $H(\mathbf{\Gamma})$ is Hamiltonian.

- The result is

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

where

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

plays role of (canonical) partition function. Using $\lim_{n\to 0}(1+an)^{1/n} = \exp(a)$, in the limit $q = 1$, standard Gibbs-Boltzmann

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

is recovered.

## Surely you're joking, Mr. Tsallis

*Before* limit is taken, properties are strange in five ways.

1. For $q \neq 1$ regime, certain points may have $p_q(\mathbf{\Gamma})$ negative or imaginary. We set probability zero there. This may be even for finite energy.

2. Equally foreign, when $q \neq 1$, relative probability of two points depends on choice of zero of energy. By defining

$$\bar{H}(\mathbf{\Gamma}) = \frac{1}{\beta(q-1)} \ln\left[1 - (1-q)\beta H(\mathbf{\Gamma})\right] \tag{6}$$

   probability at $\mathbf{\Gamma}$ takes familiar form:

$$p(\mathbf{\Gamma}) = \frac{1}{Zh^{dN}} \exp(-\beta \bar{H}(\mathbf{\Gamma})) \tag{7}$$

3. However, for constant shift $\epsilon$, relative probability

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

depends on $\epsilon$!

4. A way out is to rewrite ratio

$$\frac{p_q(\mathbf{\Gamma}_{\rm new})}{p_q(\mathbf{\Gamma}_{\rm old})} = \left[\frac{1-(1-q)\beta' H(\mathbf{\Gamma}_{\rm new})}{1-(1-q)\beta' H(\mathbf{\Gamma}_{\rm old})}\right]^{\frac{1}{1-q}} \tag{9}$$

and absorb $\epsilon$ in effective "temperature"

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

In $q = 1$ limit, effective temperature equals standard temperature. Otherwise, adding potential shift $\equiv$ rescale temperature.

5. Equilibrium averages calculated using weighting by probability $p_q(\mathbf{\Gamma})$ of Eq. (3) raised to the power of $q$ (required by the generalized statistical mechanics).

6. The so-called q-expectation value is written

$$\langle \ldots \rangle_q = \int [p_q(\mathbf{\Gamma})]^q \ldots d\mathbf{\Gamma}. \tag{11}$$

In general, $\langle 1 \rangle_q \neq 1$ for $q \neq 1$. Clearly, an odd "average!" Also

inconvenient: requires $Z_q$.

7. Is "temperature" $1/\beta$ related to the variance of momentum as in classical equipartition theorem? No simple generalization of equipartition theorem. For the 2N dimensional phase space $\mathbf{\Gamma} = (x_1 \ldots x_N, p_1, \ldots p_N)$ ensemble average of *harmonic* system is

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

For $q = 1$, standard result $\langle p_k^2 \rangle = 1/\beta$. In general, average proportional to $1/\beta$ but not equal to it. Situation equally strange for unnormalized "multifractal" average where

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

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

Distribution of momenta cannot be written as a product of single

particle distributions

$$\langle p_k^2 + p_k^2 \rangle_q \neq 2\langle p_k^2 \rangle_q. \tag{14}$$

No linear scaling of momentum variance with degrees of freedom.

8. When $q = 1$, can use extensivity of entropy to derive Boltzmann entropy equation $S = k \ln W$ (microcanonical ensemble). When $q \neq 1$, odd property that the generalization of the entropy $S_q$ not extensive leads to peculiar form of probability. Non-extensivity of $S_q$ has led to speculation that Tsallis statistics applicable to gravitational systems where interaction length scales comparable to the system size violate the assumptions underlying Gibbs-Boltzmann statistics (Maddox, 1993)

# Ideal systems

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

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

partition function:

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

where $\Lambda = \sqrt{h^2\beta/2\pi m}$ thermal wavelength of $k$th oscillator.

- For an ideal gas ($U = 0$)

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

where $L$ length of box with ideal gas. For $q \to 1$ use asymptotic

approximation $\Gamma(x+a)/\Gamma(x+b) = x^{a-b}$, (for large $x$) to show recovery of standard partition function ideal gas.

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

- Now N 1-d harmonic oscillators with Hamiltonian

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

- Canonical partition function:

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

- Configuration integral can be evaluated and partition function is

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

- Note no unique separation $Z_q = Z_q^{\text{trans}} Z_q^{\text{vib}}$. However, using result

for the ideal gas translational partition function

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

- In the limit $q \to 1$:

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

and Gibbs-Boltzann canonical partition function recovered.

## Ensemble averages and the "q-expectation value"

For certain $q$'s and harmonic potential, distribution $p_q(\mathbf{\Gamma})$ can have infinite variance (Cauchy). This motivated use of **$q$-expectation value** to compute average as

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

To avoid $\langle 1 \rangle_q \neq 1$ and need to compute $Z_q$ to average, we employed different generalization of canonical ensemble average

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

which is obviously normalized.

- With new definition, integrate over momenta to get

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

Useful: not necessary to evaluate the partition function to average. (Difficult to compute partition function numerically by importance sampling.) Will lead to feasible algorithms.

## Monte Carlo methods for pure Tsallis statistics

Configurational Monte Carlo algorithm based on uniform random trial moves and acceptance probability

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

where $p_q(\mathbf{r}) \propto [1-(1-q)\beta U(\mathbf{r})]^{\frac{1}{1-q}}$, samples for Eq. (26). Such Monte Carlo algorithm used to compute averages for Tsallis statistical distribution.

- In thermodynamic limit (large $N$) for $q \neq 1$ we find acceptance probability $= 1$ for even the largest $\Delta U$. Effectively, Monte Carlo sampling reduces to random walk on $U$ landscape. Can use this to devise a sampling scheme to overcome **broken ergodicity**. Only part-time acceptance in Eq. (27), rest spent sampling by standard Metropolis criterion. (q-jumping)
- Alternatively, use MC with uniform trial moves and acceptance

probability

$$p = \min\left[1, \left(\frac{p_q(\mathbf{\Gamma}_{\rm new})}{p_q(\mathbf{\Gamma}_{\rm old})}\right)^q\right] \tag{28}$$

to sample $[p_q(\mathbf{\Gamma})]^q$. In thermodynamic limit, no peculiar behavior. Moreover, an algorithm of this sort can be used to calculate standard, Gibbs-Boltzmann ($q = 1$) equilibrium averages

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

Proper $q = 1$ equilibrium calculated over trajectory sampling for $q \neq 1$ (with advantage of enhanced sampling for $q > 1$).

# Chemical equilibrium

Bistable system (reactant-product)

$$\alpha \rightleftharpoons \gamma. \tag{30}$$

Equilibrium constant

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

where $X_\alpha$ and $X_\gamma$ mole fractions of reactants and products,
Heaviside functions $\theta_\alpha(\mathbf{\Gamma})$ and $\theta_\gamma(\mathbf{\Gamma})$

- If barrier $>> kT$, expand potential using a harmonic approximation to the $\alpha$ and $\gamma$ potential wells. For the $\alpha$ state well

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

Equilibrium constant low temperature equilibrium constant is

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

If $q \neq 1$, equilibrium distributions are more delocalized and low temperature approximation may not be well justified.

## Transition state theory for rates of barrier crossing

TST upper bound on rate of transition between states.
Assumption of theory: once reactant acquires energy to cross barrier, it will cross the transition and deactivated as product.
What is TST rate constant in Tsallis statistics?

- Need **not** know dynamics of $p$ but only equilibrium.

  For bistable potential with TS at $x = x^{\ddagger}$, the TST rate for forward reaction is

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

  where $p_q(\mathbf{\Gamma}) = p_q(x, v)$ is generalized statistical distribution

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

with

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

and $H(x,v) = mv^2/2 + U(x)$ Hamiltonian.

- TST rate constant

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

where

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

- 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 rate constant

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

- As expected, limit $q \to 1$ gives standard TST result

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

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

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

  independent of the temperature (even when T=0)!

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

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

## Temperature scaling in simulated annealing

Using TST results, can derive scaling relation in simulated annealing **optimization** protocol.

- Suppose relevant energy scales of $U(\mathbf{r}^N)$ bounded by $\Delta U$ = the difference in energy between the ground and first excited state minima, and $U^\ddagger$ = highest barrier accessed from global energy minimum. Final temperature (maximum $\beta$) reached in simulated annealing run must be small enough so mole fraction in the **global** energy minimum is significant. In other words, based on Eq. (33) we demand that $K_{eq}^{\max} = K_{eq}(\beta_{\max}; q)$.
- Time trajectory must spend at $\beta_{\max}$ to ensure equilibrium distribution sampled is at least $\tau_{min}$, the time required to surmount largest barrier separating the global from other minima. Using Eq. (39), find

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

where

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

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

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

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

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

# Maxwell-Tsallis statistics

We developed MC algorithms based on sampling Tsallisian distributions. Using acceptance probability

$$p = \min\left[1, \left(\frac{p_q(\mathbf{r}^N_{\rm new})}{p_q(\mathbf{r}^N_{\rm old})}\right)^q\right]. \tag{46}$$

detailed balance

$$[p_q(x)]^q W(x \to x') = [p_q(x')]^q W(x' \to x) \tag{47}$$

is satisfied where $W(x, x')$ transition matrix.

- The walk generated by Eq. (28) samples the distribution

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

- This probability can be found by extremizing generalization of

entropy Eq. (1) subject to the constraints

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

# Hybrid Monte Carlo algorithm

- Implement a hybrid MD/MC method composed
  1. Velocities are randomly chosen from a Maxwell distribution at a given temperature.
  2. The positions and velocities are updated for a time step $\Delta t$ 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

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

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

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

  4. Return to 1.

- When integrator reversible and symplectic, acceptance exactly satisfies detailed balance and the walk samples equilibrium distribution $[p_q(\mathbf{r}^N)]^q$.
- Similar algorithm used to sample the equilibrium distribution $[p_q(\mathbf{r}^N)]^q$ in the conformational **optimization**. When $q > 1$, conformational sampling greatly enhanced over standard Metropolis MC. In this form, the velocity distribution can be thought to be Maxwellian.

## Molecular dynamics with an effective potential

- MC algorithm generates

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

- Define effective potential $\mathcal{W}_q(\mathbf{r}^N;\beta)$

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

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 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

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

for particle of mass $m_k$ and position $\mathbf{r}_k$ and $\bar{U}$ defined by Eq. (51).

Constant-temperature molecular dynamics algorithm generates $P_q(\mathbf{r}^N)$.

- Effective force derived from the effective potential $\mathcal{W}(\mathbf{r}^N)$ has interesting properties. $F_q(\mathbf{r}^N;\beta) = -\nabla_{\mathbf{r}_k}\bar{U} = F_1(\mathbf{r}^N)\alpha_q(\mathbf{r}^N;\beta)$ where $F_1(\mathbf{r}^N)$ is "exact" force for standard MD ($q = 1$) 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.
- 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, $\alpha_q(\mathbf{r}^N,\beta)$ small. It may surprise you that for the function to be well defined, $\beta U$ 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.

# Rate and equilibrium constants

Once again carry out integral in low T approximation

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

Equilibrium constant is

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

In the limit $q \to 1$, standard TST:

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

recovered.

- Return to more general expression, in low temperature limit TST

estimate of rate is

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

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

- For special case of $q = 2$ find

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

- For $q = 1$, normal TST rate independent of $T$ at high $T$ and varies exponentially with $T$ in the limit $kT << U^\ddagger$ as

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

- 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

$$k_{TST} \sim \beta^{-1/2} \tag{61}$$

independent of $q$! As $q \to 1$ exponential (Arrhenius) T dependence recovered. However, for larger values of $q$ temperature scaling of rate is weak inverse power law. At all temperatures, the TST rate is significantly larger for $q > 1$ than for $q = 1$.

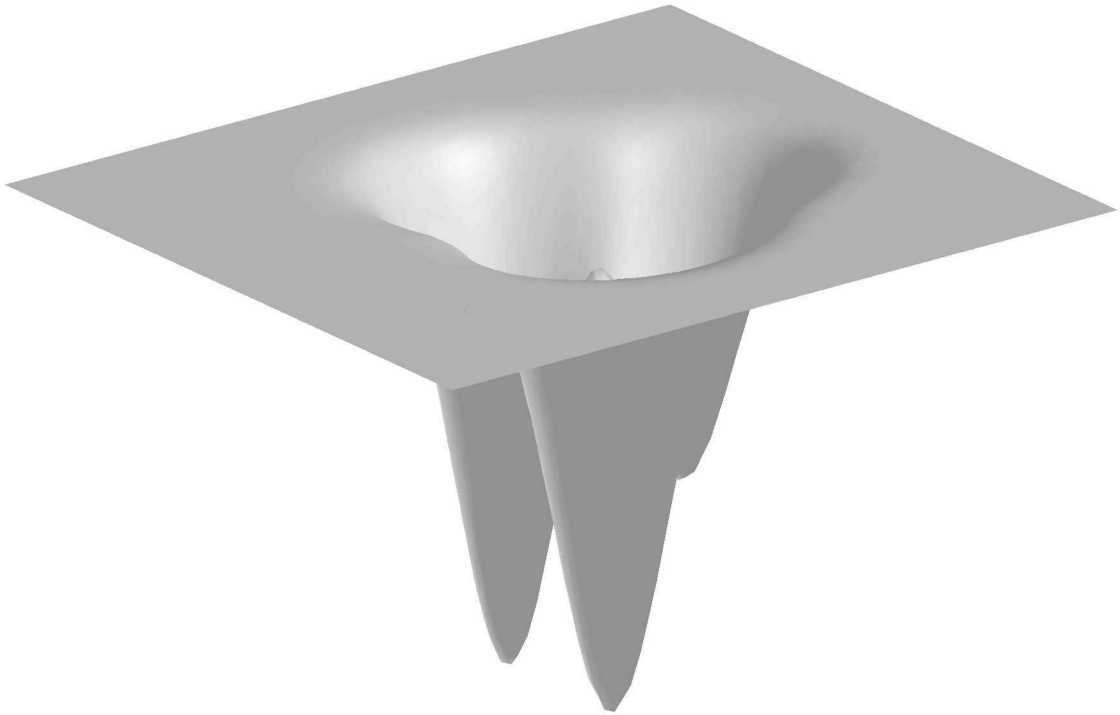

*Fig. 1 The two-dimensional potential considered in the text has two deep holes, seen in the front and left sides of the plot, and a less deeper hole to the right.*

- Relaxation of a system to equilibrium can be modeled using a master equation

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

- Elements of the transition matrix from state $j$ to state $i$ can be estimated in the transition state theory approximation

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

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

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

- The symmetric transmission coefficients are defined $B_{ij} = L_{ij} M_i$.

The general solutions are of the form

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

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

- Calculate 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.
- One of the three eigenvalues is zero, for any $q$, for reasons of conservation of probability.
- 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.

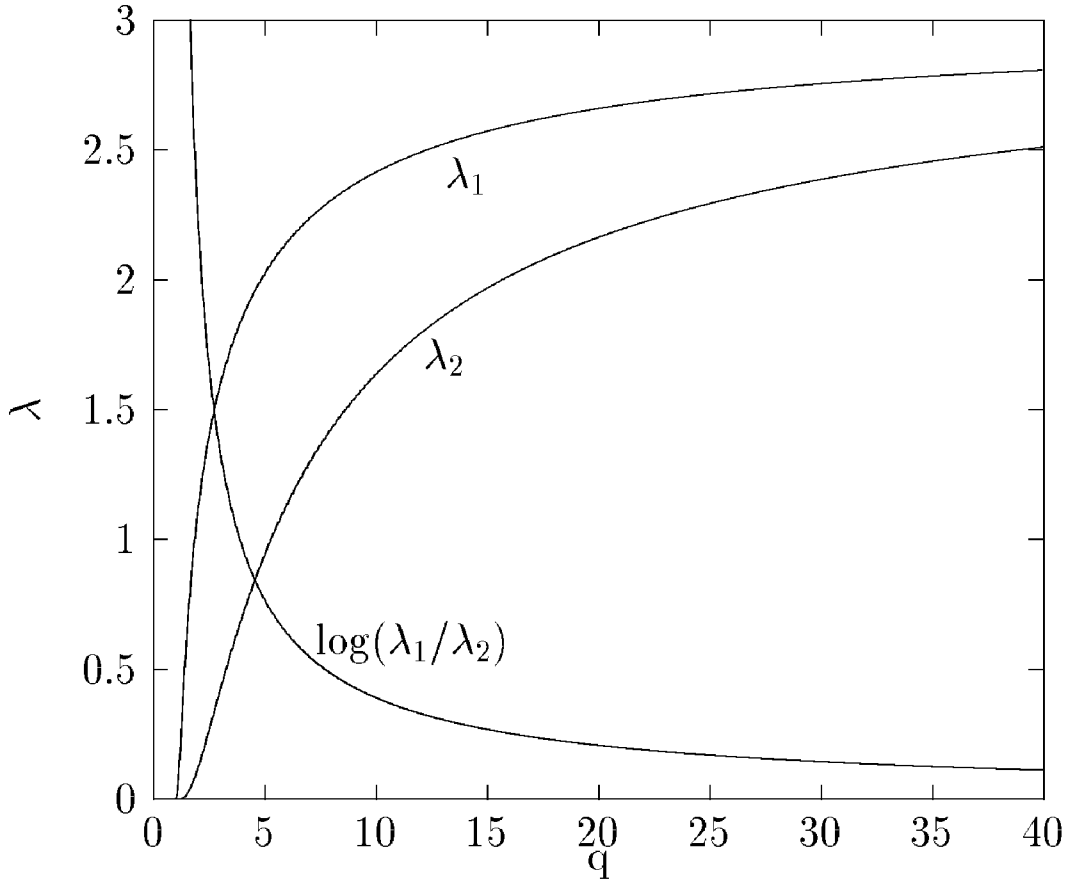


*Fig. 2 The dependence on q of the non-zero eigenvalues of the two-dimesional, three-hole model described in the text shows the rapid onset of escape from wells as soon as q exceeds unity and the saturation at higher values of q. Also shown is the logarithm of the ratio of the two non-zero eigenvalues.*

- 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 shown to lead to anomalous diffusion and Lévy flights in the $5/3 < q < 3$ regime (Tsallis, 1995)
- Due to delocalized nature of equilibrium distributions, might find that microstates of master equation are not well defined. Even at low $T$, it may be difficult to identify distinct microstates.
- Same delocalization can lead to large transition probabilities for states not adjacent in configuration space. This would violate assumption 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.
- However: 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.(Zwanzig 1995)