Letter

Anomalous velocity distributions in slow quantum-tunneling chemical reactions

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Recent work [R. Wild *et al.* Nature **615**, 425 (2023)] has provided an experimental break-through in the realization of a quantum-tunneling reaction involving a proton transfer. The reaction $D^- + H_2 \to H^- + HD$ has an extremely slow reaction rate as it can happen only via quantum tunneling, thus requiring an extremely large density of the reactants in the ion trap. At these high densities strong deviations from Maxwell-Boltzmann statistics are observed. Here we develop a consistent generalized statistical mechanics theory for the above nonequilibrium situation involving quantum effects at high densities. The trapped ions are treated in a superstatistical way and a q-Maxwellian velocity distribution with a universal dependence of the entropic index q on the density n of the buffer gas is derived. We show that the velocity distribution of the ions is non-Maxwellian, more precisely q-Gaussian, i.e., $p(v) \propto v^2[1 + (q-1)\tilde{\beta}v^2]^{1/(1-q)}$, with entropic index $q > 1$ depending on the density n of H_2 molecules, in excellent agreement with the experimental observations of Wild *et al.* Our theory also makes predictions on the statistics of temperature fluctuations in the ion trap which can be tested in future experiments. Through the superstatistical approach, we obtain an analytical expression for $q(n)$ which is consistent with the available experimental data, and which yields $\lim_{n\to 0} q(n) = 1$, i.e., recovering the Maxwell-Boltzmann distribution in the ideal gas limit, as well as $\lim_{n\to\infty} q(n) = 7/5$.

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Ordinary chemical reactions are usually described by ordinary statistical mechanics, that is to say the reactants obey Boltzmann-Gibbs (BG) statistics. The time evolution of ordinary chemical reactions is described by the Arrhenius law, which is in turn grounded on BG statistical mechanics. Consequently, when the reaction occurs, say in a gas in a container of large volume, the distributions of velocities of the various chemical components are of the celebrated Maxwellian (Gaussian) form. In a typical picture for such a reaction, the system is initially at the bottom of a local minimum of a potential energy well and, by overcoming an activation barrier, it ends up in a global minimum. The situation, however, is quite different in modern state-of-the-art experiments based on ion traps. Here the assumption of Maxwell-Boltzmann statistics has been shown to be inherently violated [1–4]. This is due to the fact that the reactants are usually confined in a very small volume, so that temperature fluctuations occur and nonequilibrium effects play an important role. Also, the usual assumption of a small density (which makes kinetic theory applicable) can be inherently violated, so that intrinsic quantum effects play an important role. Moreover, the ions are constantly driven by an external field, so that their temperature, due to rf (radio frequency) driving, is usually larger than that of the embedding neutral buffer gas, a nonequilibrium situation. There is also heat loss in the system due to the possibility of some ions vanishing from the trap.

As an example of a recent ground-breaking experiment in this direction, where the assumption of Maxwell-Boltzmann statistics is inherently violated, let us consider the experiment described in [5] (for other, more general experiments, see, e.g., the recent review [6]). This experiment deals with the reaction $D^- + H_2 \to H^- + HD$ and it is ground-breaking because it reaches a much higher density of reactants than previous ion-trap experiments. In the above reaction a proton transfer occurs, however the rate constant is extremely small so that a very high density of reactants is needed to see a measurable effect. This high density was achieved in [5] and the reaction was actually experimentally observed for the first time. Consequently, due to the high density, very sensitive quantum effects are dominant in this ultra confined driven system at low temperatures. Moreover, quantum tunneling transitions rather than classical transitions can be experimentally studied for this system, which provide the dominant pathway to enable the reaction at smaller densities [7–11].

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Interestingly enough, but understandable due to the small volume and high density of the driven system, the distribution of velocities v of the ions was shown (see, e.g., Fig. 3(c) of [5]) to be anomalous, in the sense that it has a q-Maxwellian form, instead of the *a priori* expected Maxwellian form $p(v) \propto v^2 e^{-\frac{\beta}{2}mv^2}$. The three-dimensional q-Maxwellian velocity distribution is given by

$$p_q(v) \propto v^2 e_q^{-\frac{\beta_q}{2}mv^2}, \tag{1}$$

where the q-exponential function is defined as

$$e_q^z \equiv [1+(1-q)z]^{\frac{1}{1-q}} = \frac{1}{[1-(q-1)z]^{\frac{1}{q-1}}} \quad \left(q \geqslant 1;\ e_1^z = e^z\right). \tag{2}$$

These distributions maximize the q-entropies S_q [12] subject to suitable constraints. In the following we will derive the above distributions in the given experimental context. A particular highlight will be that we will obtain a theoretical prediction how the entropic index q in the generalized statistical mechanics description [12–14] depends on the density n of H_2 molecules. Our approach will be based on superstatistics [15–17] and ultimately we will derive an area-law for the entropic index $q-1$.

Superstatistical techniques have been applied to a variety of nonequilibrium problems in the past 24 years [15–30]. In [18–20] entropic approaches to superstatistics were discussed, introducing more general entropy measures that reproduce the superstatistical distributions under maximization. The relaxation and diffusion properties of superstatistical systems were discussed in [21–23]. Applications of the superstatistics concept have been reported for a variety of complex systems, for example for Lagrangian turbulence [24,25], for biological diffusion processes [26], and also for fluctuations occurring in renewable energy systems and power grids [27–29].

The relevance of superstatistics in the context of ion trap experiments was previously emphasized in [3]. In that paper small densities of reactants were assumed so that kinetic theory is applicable. Here we further develop the theory and extend it to the case of large densities, which is necessary to understand experiments such as the recent one described in [5]. Our main result is a generally applicable thermodynamic superstatistical theory that correctly describes the behavior of quantum tunneling reactions in ion trap experiments at very high and very small densities alike.

Our aim in the following is to obtain a nonequilibrium statistical physics understanding how the entropic index q depends on the density n of the H_2 particles involved. Clearly, as the quantum-tunneling reaction has a very small reaction rate, a very high density n is required to produce a measurable effect. Keeping the number of particles constant, a very high density corresponds to a very small volume V. It is here where the superstatistical approach comes into play [15–17]: In a very small volume we expect temperature not to be constant but there will be temperature fluctuations, meaning $\beta = 1/kT$ becomes a random variable (see Fig. 1).

We may associate these temperature fluctuations either with classical fluctuations (heat losses through the surface) or with quantum fluctuations (uncertainties of the temperature)

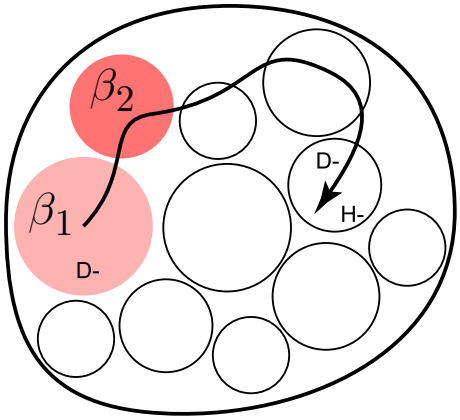

FIG. 1. The basic idea of superstatistics. The spatial region in which the reactants are contained consists of several subregions of inverse temperature $\beta_1, \beta_2, \beta_3, \ldots$ through which the molecules move. Each subregion is temporarily in local thermal equilibrium at local temperature β_i^{-1}. For a superstatistical description to be valid, there must be a clear time scale separation in the system, i.e., the relaxation to local equilibrium must be faster than the typical time scale of temperature variations. See [30] for details on how to extract these parameters from experimentally measured time series.

that are allowed due to the uncertainty relation. In the χ^2 superstatistics approach, introduced in [16] and applied to ion traps in [3], one assumes the following form for the inverse temperature random variable:

$$\beta = \sum_{i=1}^{\mu} X_i^2. \tag{3}$$

Here the X_i are Gaussian random variables with mean 0, which are squared in order to produce a positive contribution to $\beta = 1/kT$. It must be a positive contribution since β must always be positive. The number μ is an effective number of degrees of freedom that contribute to the temperature fluctuations.

Let us now consider a very small volume (equivalent to a very large density), where the density is so large that quantum effects start to dominate and nonequilibrium effects are dominant, meaning there are big temperature fluctuations. We expect the fluctuations of β to be dominated by the heat loss flow through the surface of the given small volume, for the three spatial dimensions in which the experiment is performed. In addition, we may allow for an additional explicit time dependence of the temperature in a given volume. We thus arrive at the result that at the highest experimentally possible densities $n_{\max}$ that are achievable in the experimental setup the number μ of degrees of freedom describing the temperature fluctuations is given by $\mu = 4$, with 3 degrees of freedom corresponding to space and 1 degree to time, so that

$$\beta = X_1^2 + X_2^2 + X_3^2 + X_4^2. \tag{4}$$

This formula is only valid at the highest experimentally achievable densities $n_{\max}$, i.e., the smallest possible volume. If the density decreases, which is equivalent to the volume increasing (keeping the particle number constant), we then expect more degrees of freedom to enter the system, as heat can flow in all kinds of local directions, but only the losses

through the surface that includes all reactants are relevant. Because of this surface effect, we expect the number μ of degrees of freedom to grow as

$$\mu \sim V^{\frac{2}{3}} \sim n^{-\frac{2}{3}} \tag{5}$$

since the surface of the system (through which the heat losses occur) generally goes like volume V to the power 2/3. At the highest possible density $n_{\max}$ achievable in the experiment we have $\mu_{\min} = 4$. Thus, as $n \sim V^{-1}$, we arrive at the scaling formula

$$\mu = 3 \cdot \left(\frac{V}{V_{\min}}\right)^{\frac{2}{3}} + 1 = 3 \cdot \left(\frac{n_{\max}}{n}\right)^{\frac{2}{3}} + 1, \tag{6}$$

which is a formula that provides us with the effective degrees of freedom μ of the temperature fluctuations as a function of the density n of the quantum reactants.

Let us now do superstatistics [15–17] (i.e., we consider averaging over the fluctuating inverse temperatures, weighted with a probability density function $f(\beta)$ to observe a particular β, see Appendix section for more details). Assume we know the inverse temperature β as given in a particular spatial region at a particular time. Then at this point we have local Maxwell Boltzmann statistics

$$p(E|\beta) = CEe^{-\beta E}, \tag{7}$$

where $E = \frac{1}{2}mv^2$ is the kinetic energy of the reactant, $p(E|\beta)$ is the conditional probability to observe an energy state E given the local environment with inverse temperature β. The normalization constant C is readily obtained from

$$\int_0^\infty p(E|\beta)dE = 1 \tag{8}$$

to be

$$C = \beta^2. \tag{9}$$

Due to the temperature fluctuations in the system, we need to average over all states of the inverse temperature variable β, weighted with the probability density $f(\beta)$ to observe a particular β, to obtain the marginal distribution

$$p_q(E) = \int_0^\infty d\beta\ f(\beta)p(E|\beta). \tag{10}$$

In our case, from the assumption that β is given by Eq. (3), we immediately identify $f(\beta)$ as the χ^2 distribution with μ degrees of freedom:

$$f(\beta) = \frac{1}{\Gamma\left(\frac{\mu}{2}\right)}\left(\frac{\mu}{2\beta_0}\right)^{\frac{\mu}{2}} \beta^{\frac{\mu}{2}-1} \exp\left(-\frac{\mu}{2}\frac{\beta}{\beta_0}\right), \tag{11}$$

where

$$\beta_0 = \langle\beta\rangle = \int_0^\infty \beta f(\beta)d\beta = \mu\langle X_i^2\rangle \tag{12}$$

is the average inverse temperature in the system, and the variance of inverse temperature fluctuations is given by

$$\langle\beta^2\rangle - \beta_0^2 = \int_0^\infty \beta^2 f(\beta)d\beta - \beta_0^2 = \frac{2}{\mu}\beta_0^2. \tag{13}$$

The distribution (11) represents one of three possible universality classes that are usually considered in the superstatistics approach [17], and its relevance in the context of ion trap experiments was recently derived in [3] where it was shown that it arises from a recurrence relation for temperature due to subsequent collisions of the ions.

Let us now explicitly do the integration in Eq. (10), using Eqs. (7), (9), and (11). The result of a short calculation (see Appendix section for details) is

$$p_q(E) = \int_0^\infty d\beta f(\beta)\beta^2 Ee^{-\beta E} \sim Ee_q^{-\tilde{\beta}E}, \tag{14}$$

where

$$q = 1 + \frac{2}{\mu + 4} \tag{15}$$

and

$$\tilde{\beta} = \frac{\beta_0}{1 - 2(q-1)}. \tag{16}$$

In other words, the integration over the fluctuating temperature states of the system containing the reactants quite naturally leads to q-exponential distributions. We have thus clarified how the nonequilibrium situation of the small volume of reactants with a high density and temperature fluctuations (as sketched in Fig. 1) leads to the actually observed q-Maxwellian distributions. While the superstatistics model as such is classical, strong temperature fluctuations only occur for very dense systems in small volumes, where quantum effects start to dominate. For this reason, quantum effects are (indirectly) very relevant in this problem and they correspond to small finite values of μ.

The dependence of the q-parameter on the density n of reactants can now be predicted by combining Eq. (15) with Eq. (6). We obtain the formula

$$q - 1 = \frac{2}{\mu(n) + 4} = \frac{2}{3\left(\frac{n_{\max}}{n}\right)^{\frac{2}{3}} + 5}. \tag{17}$$

This formula, within the estimated error bars, is in good agreement with the experimental results (see blue curve in Fig. 2). The two experimental data points in Fig. 2 correspond to the measurements and simulations published in Fig. 3(c) of [5], the corresponding q-values and densities were discussed in [32]. The error bars were estimated from the dispersion of the data.

Let us discuss a few special cases.

(1) For $n \to 0$ we have $q \to 1$. This makes physical sense. For small densities of reactants, ordinary statistical mechanics described by $q = 1$ is recovered.

(2) For $n = n_{\max}$, we obtain $q = \frac{5}{4} = 1.25$. This is the case where the density n takes on the largest achievable value $n_{\max}$ that is reachable in the experiment. In this case there are strong temperature fluctuations in the system, and heat losses occur through the three directions of space of the smallest possible elementary reaction volume $V_{\min}$. We also allow for an explicit time dependence of the temperature, making the total number of degrees of freedom contributing to the fluctuations of temperature to be $\mu = 4$.

(3) Although not experimentally achievable, we may formally consider the limit $n \to \infty$ of infinite density. In this case formally the system is reduced to a 1-dimensional point system that is infinitely concentrated and has only one degree

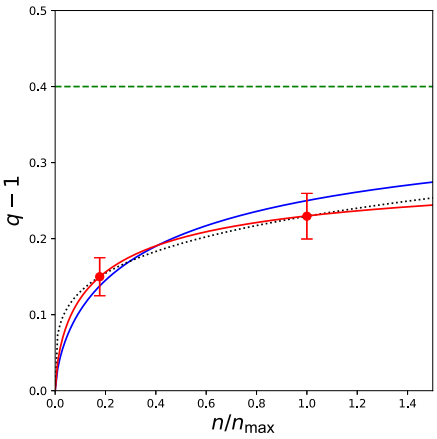

FIG. 2. Entropic index $q-1$ describing quantitatively the deviation from BG statistics as a function of the density n of reactants. The two red data points correspond to the experimental values as provided in Fig. 3(c) of [5]. The dotted curve corresponds to the heuristically conjectured $(q-1) \propto n^{1/4}$ $(n \to 0)$ of [31]; this curve exactly passes through the two (red) experimental points by construction. The blue curve corresponds to Eq. (17) $[(q-1) \propto n^{2/3}$ $(n \to 0)]$ analytically deduced within the present superstatistical approach, and expected to hold under idealized conditions. For the blue curve, $\lim_{n\to\infty} q(n) = 7/5$ (green dashed line); for $q \geqslant 7/5$, $\langle v^2 \rangle$ diverges. The red curve is the theoretical prediction of Eqs. (24) and (25), adjusting the two nonuniversal fitting constants $C_1 = 2.14$ and $C_0 = 2.56$ to their optimum values for the given experiment.

of freedom left, the explicit time dependence of the temperature. This limit leads to $\mu = 1$ and the resulting q-value is $q = q_\infty = \frac{7}{5} = 1.4$.

Interesting enough, $q = \frac{7}{5}$ as discussed under point 3 above, is precisely the limit value up to which the variance of the velocity v of the particles still exists. This can be seen as follows: We have, for the q-Maxwellian distributions,

$$p_q(v) \sim v^2 e_q^{-\tilde{\beta}\frac{1}{2}mv^2} \sim v^{2-\frac{2}{q-1}} \quad (v \to \infty). \tag{18}$$

Hence, for the integral defining the second moment of velocity v

$$M_2 = \langle v^2 \rangle = \int_0^\infty v^2 p_q(v) dv \tag{19}$$

the integrand decays as $v^{4-\frac{2}{q-1}}$ for large v, and hence the 2nd moment M_2 only exists if

$$q < q_\infty = \frac{7}{5} \tag{20}$$

as for q-values smaller than $\frac{7}{5}$ the integrand decays stronger than v^{-1} and is thus integrable. We obtain the interesting result that our value of $q_\infty = \frac{7}{5}$, obtained previously from the $n \to \infty$ asymptotics of the formula (17), coincides precisely with the point up to which the variance of the velocity distribution exists.

Next, we deal with the effective temperature parameter of the system of quantum reactants. This is described by the parameter β_q in Eq. (1), and in the superstatistics approach the same parameter is usually denoted as $\tilde{\beta}$. The parameter β_q has a nontrivial q-dependence (and thus density dependence) which we can derive by combining Eq. (16) and Eq. (15) with Eq. (6). We ob tain by putting Eq. (6) into Eq. (16)

$$\beta_q \equiv \tilde{\beta} = \beta_0 \cdot \frac{3\left(\frac{n_{\max}}{n}\right)^{\frac{2}{3}} + 5}{3\left(\frac{n_{\max}}{n}\right)^{\frac{2}{3}} + 1}. \tag{21}$$

This yields an interesting experimentally testable prediction for the generalized statistical mechanics describing the slow quantum-tunneling reaction in the ion trap experiment: The effective inverse temperature parameter in the q-Maxwellian distribution becomes density dependent. Whereas for $n \to 0$ we have $\beta_q = \beta_0$, i.e., ordinary statistical mechanics, for $n \to n_{\max}$ we obtain $\beta_q \to 2\beta_0$. If we interpret β_0^{-1} as the physical average temperature of the ions (which are in fact in a nonequilibrium situation with fluctuating temperature) and if we then fix the temperature parameter $\tilde{\beta} = \beta_q$ to be used in the q-Maxwellian distribution from the temperature of the embedding H_2 gas (which is having no temperature fluctuations) then the temperature β_0^{-1} can be interpreted as the average temperature of the ions and β_q^{-1} as the fixed temperature of the embedding H_2 gas. Clearly, the ion temperature is larger than the H_2 bath temperature for any $q > 1$. This is a direct consequence of Eq. (15), which we may write in terms of the temperature parameters as

$$T_{\text{ion}} = \frac{1}{1-2(q-1)} T_{\text{bath}}. \tag{22}$$

For example, for $n = n_{\max}$ (equivalent to $q = \frac{5}{4}$) we obtain the result that the ion temperature is larger by a factor 2 than the H_2 bath temperature. This tendency is in agreement with observations: The ion temperature is always observed to be bigger than the bath temperature in the ion trap experiments. The physical interpretation is that this is due to rf heating.

We may finally use standard formulas from superstatistics to estimate the size of temperature fluctuations for the ion gas. Equation (13) implies that the degrees of freedom μ fix the variance of inverse temperature fluctuations according to the general formula

$$\frac{\langle \beta^2 \rangle - \beta_0^2}{\beta_0^2} = \frac{2}{\mu(n)}. \tag{23}$$

This formula yields at the measured experimental density $n = 4.8 \times 10^{14}\text{cm}^{-1}$ (the red data point on the left in Fig. 2) the value $\mu \approx 10.5$ and thus $\delta\beta/\beta = \delta T/T \approx 0.44$. The authors of [5] do not provide precise temperature or temperature fluctuation measurements but just mention in their paper that the temperature of the ions in their experiments is roughly given given by $T = (15 \pm 5)$ Kelvin, i.e., they indicate a rather large uncertainty in temperature given by ± 5 Kelvin. Apparently the order of magnitude of their stated $\delta T/T \approx 5/15 = 0.33$ coincides with the order of magnitude predicted by our superstatistical theory. In fact, ion trap experiments are usually plagued by large uncertainties in temperature, which we have now identified in this work as a fundamental nonequilibrium quantum effect, rather than an imperfection of the experiment. In a sense, our theory presented is a classical theory of temperature fluctuations, which is relevant for high-density quantum reactant systems of small volume. The predictions of our theory can be checked by ion-trap experiments where the

reactants exhibit quantum-tunneling reactions of very small reaction rates, so that very high densities are necessary to trigger the quantum-tunneling process.

In general, each realistically achievable ion trap experiment will have its own equation of state $q = q(n)$, which could be experimentally measured. A more general theory, derived in the Appendix section, predicts the formula

$$q - 1 = \frac{2}{\mu(n) + 4} \tag{24}$$

with

$$\mu(n) = C_1 \cdot \left(\frac{n_{\max}}{n}\right)^{\frac{2}{3}} + C_0, \tag{25}$$

where C_1 and C_0 are two nonuniversal constants that depend on the experimental setup. Also the temperature fluctuation statistics could and should be investigated in future experiments. The experimental details enter into the value represented by the constants C_0 and C_1, which are nonuniversal and which depend, e.g., on the Mathieu stability parameters of the Mathieu differential equation describing the ion trap, as well as the mass ratios of the neutral particles and ions. However, the exponent $2/3$ describing the area law is expected to be universal [33–36]. The function $q(n)$ with the given C_0 and C_1, in turn, fixes the statistics of the temperature fluctuations in the experimental system via Eq. (23). The effective entropy S_q describing this scale-dependent system has nonadditive properties [37] (see the Appendix section for more details).

Our approach presented here concentrated onto the statistical description of the fluctuating heterogeneous environment containing the reactants that take part in the quantum tunneling process. The actual quantum tunneling process as such has been theoretically dealt with in [11] and temperature-dependent rate coefficients $\lambda(\beta)$ were calculated in that paper. In the future, it would be interesting to provide a superstatistical generalization of the quantum tunneling theory of Yuen *et al.* [11], by considering the strong temperature fluctuations in the experimental system and by proceeding to superstatistical averages of rate constants given by $\bar{\lambda} = \int_0^\infty f(\beta)\lambda(\beta)\,d\beta$.

To conclude, in this Letter we have developed a generalized statistical mechanics theory based on a superstatistical approach that gives quantitative predictions how the entropic index q depends on the density n of reactants in slow quantum-tunneling reactions. Future ion trap experiments, varying in a systematic way the very high density of reactants, will be able to quantitatively test the predictions of our theory with high precision. The index $q = q(n)$ is relevant for both the shape of the anomalous velocity distributions as well as the statistics of temperature fluctuations in the system.

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Appendix: Type-A versus Type-B superstatistics. The averaging of the Boltzmann factors can be done in two different ways, either excluding the normalization constant $Z(\beta)$ or including it. This is usually referred to as type-A or type-B superstatistics [16]. For type-A superstatistics one simply considers averaged (unnormalized) Boltzmann factors of the form

$$B(E) = \int_0^\infty f(\beta)e^{-\beta E}d\beta. \tag{26}$$

In our letter here, however, we use type-B superstatistics which is different from type-A superstatistics. Type-B is generally more physical since it basically corresponds to an application of Bayesian statistical methods for the local statistical mechanics, taking into account the proper normalization. Given some probability density $f(\beta)$ of inverse temperatures β and some energy level E corresponding to an arbitrary Hamiltonian H one defines marginal probability densities in type-B superstatistics as

$$p(E) = \int_0^\infty f(\beta)\frac{1}{Z(\beta)}e^{-\beta E}d\beta, \tag{27}$$

where $Z(\beta)$is the partition function of the local statistical mechanics. For $f(\beta)$ all kinds of probability densities can be used, but q-statistics as observed in ion trap experiments requires the χ^2-distribution

$$f(\beta) = \frac{1}{\Gamma(\frac{\mu}{2})}\left(\frac{\mu}{2\beta_0}\right)^{\frac{\mu}{2}}\beta^{\frac{\mu}{2}-1}\exp\left(-\frac{\mu}{2}\frac{\beta}{\beta_0}\right), \tag{28}$$

where

$$\beta_0 = \langle\beta\rangle = \int_0^\infty \beta f(\beta)d\beta = \mu\langle X_i^2\rangle \tag{29}$$

is the average inverse temperature in the system. One immediately recognizes that the integration result in Eq. (27) is influenced both by the functional form of $f(\beta)$ as well as what the local partition function $Z(\beta)$ of the local statistical mechanics is. If we assume that the β-dependence of $Z(\beta)$ is given by the functional form

$$Z(\beta) \sim \beta^x e^{-y\beta} \tag{30}$$

then, by explicit integration in Eq. (27) using $f(\beta)$ as given in Eq. (28), one obtains

$$p_q(E) = \int_0^\infty d\beta f(\beta)\frac{1}{Z(\beta)}e^{-\beta E} \sim e_q^{-\tilde{\beta}E}, \tag{31}$$

where

$$q = 1 + \frac{2}{\mu - 2x} \tag{32}$$

and

$$\tilde{\beta} = \frac{\beta_0}{1 + (q-1)(x - \beta_0 y)}. \tag{33}$$

For the ion trap dynamics, local Maxwellian statistics $Ee^{-\beta E}/Z(\beta)$ with different temperatures was assumed, which led to the normalization constant $Z(\beta) = \beta^{-2}$. Hence, $x = -2$ and $y = 0$ for the formulas used in the main part of the paper.

Generalizing the scaling theory of $q(n)$. Our generalized statistical mechanics theory developed in the main section opens the door to various intriguing new ideas and predictions that can be experimentally tested with quantum

tunneling experiments of the type performed by Wild *et al.* [5]. The first observation is that our predicted n-dependence in Eq. (17) is universal, i.e., it does only depend on the density n, and not on further parameters. This universality is expected to hold for an idealized experiment under optimum conditions. Realistically, there will be many influences that disturb this idealized setting. To take these effects into account, we may combine our universal formula with the low-density kinetic theory of ion traps developed by Rouse and Willitsch [3], by allowing for a nonuniversal additive constant in Eq. (6). In other words, we may generally write for the degrees of freedom

$$\mu(n) = 3 \cdot \left(\frac{n_{\max}}{n}\right)^{\frac{2}{3}} + C_0, \tag{34}$$

where the additive constant C_0 is nonuniversal and depends on the particular properties of the experiment, such as the mass ratio m_n/m_i or the Mathieu stability parameters of the ion trap. By this, the fundamental area-dependence law of the degrees of freedom, reflected by the exponent $\frac{2}{3}$, is still conserved. This area dependence somewhat reminds us of the area dependence of Bekenstein-Hawking entropy relevant for black holes, although this is only a formal analogy. In our case, the area dependence comes from the fact that heat is lost through the surface of the volume that contains the reactants. Note that area laws (i.e., exponents $2/3$) are also relevant in the general context of entanglement entropies [33,34]. The area dependence of the heat loss through the surface proposed in our approach here is thus consistent with the area dependence of generalized entropies describing quantum entanglement, and in general it also allows for the embedding of more general entropies describing quantum processes [35,36].

Once we allow the additive constant C_0 to take on nonuniversal values that depend on the experimental details, there is no reason to keep the multiplicative constant 3 in front of the density-dependent term in Eq. (34). In fact, every experiment performed will have a different maximum density $n_{\max}$ that can be achieved. In a sense the chosen parameter $n_{\max}$ just sets a scale to which other densities are compared to. Thus, if we fix somewhat arbitrarily some density scale $n_{\max}$, for different experiments the multiplicative constant in front of $(n_{\max}/n)^{2/3}$ will be different and will depend on the experimental details. Hence, most generally we may allow for a relation of the form

$$\mu(n) = C_1 \cdot \left(\frac{n_{\max}}{n}\right)^{\frac{2}{3}} + C_0, \tag{35}$$

where C_1 and C_0 are nonuniversal constants depending on the experimental setup. We still expect the approximate relation $C_0 + C_1 \approx 4$ to hold, since at the largest experimentally achievable densities $n_{\max}$ there are 4 space-time degrees of freedom available for the heat losses. Formula (35) still conserves the area-law of the degrees of freedom, described by the exponent $2/3$. The above function $\mu(n)$ then fixes, as before, the parameter $q-1$ as

$$q - 1 = \frac{2}{\mu(n) + 4} \tag{36}$$

and this $\mu(n)$ also enters into the temperature fluctuation statistics as given by Eq. (23). We obtain an optimum fit of the data of the experiment of Wild *et al.* [5] if we choose $C_1 = 2.14$ and $C_0 = 2.56$. This curve is shown in red in Fig. 2. Given some experimentally extracted C_0, there is then a more stringent bound on the maximum value of q that can be experimentally achieved under the given nonuniversal experimental conditions, namely $q_{\max} = 1 + \frac{2}{C_0+4}$.

Nonadditivity of S_q in the given experimental context. The present approach also allows us to give physical meaning to the nonadditivity relation of the entropic functional S_q

$$S_q(A+B) = S_q(A) + S_q(B) - (q-1)S_q(A)S_q(B), \tag{37}$$

which is generally satisfied for statistically independent subsystems A and B (see Supplemental Material for more details [38]). Here the q-entropy S_q is defined for any q as [12–14]

$$S_q = \frac{1}{1-q}\left(1 - \sum_i p_i^q\right) \tag{38}$$

and it reduces to the BG-entropy $S_1 = -\sum_i p_i \ln p_i$ for $q \to 1$. The p_i are the probabilities of the microstates i.

As the velocity distributions observed in the ion trap experiment effectively maximize the entropic functional S_q subject to suitable constraints, one may ask what the physical meaning of the relation (37) is in the given experimental context. As evidenced by the observed anomalous velocity distributions, we have $q > 1$ and hence the term proportional to $q-1$ cannot be neglected.

Our physical interpretation is as follows. We note that our scaling theory implies a temperature fluctuation statistics that is different in volumes V of different size: Volumes of bigger size have smaller temperature fluctuations. If we put together two subsystems A and B we get a different temperature fluctuation statistics (less fluctuations) as the joint system $A+B$ has bigger size. Hence, for the effective entropy describing the system there must be a negative correction term for the joint system as compared to the sum of the entropies of the two smaller subsystems. This is the physical meaning of the relation (37).

Apparently, S_q is nonadditive [37] for any given q different from 1, but if the given coupling term of strength $(q-1)$ is introduced, then the corresponding interacting field theory for the entropy is well-defined at *any* scale, and effectively takes into account temperature and quantum fluctuations that take place in a volume-dependent way. For q-statistics of the type discussed in this letter we have a bilinear interaction term of strength $-(q-1)S_q(A)S_q(B)$ (similar to a dot-product of entropic vectors for the smaller subsystems) when combining two independent subsystems A and B into a bigger subsystem $A+B$ where the temperature statistics is different due to the larger volume. The nonadditivity relation of S_q as given by Eq. (37) indeed represents one of the simplest interacting field theories of entropy one can think of, where temperature fluctuations are described in an effective way, although other types of superstatistics [16,17] or other types of entropies [14,33–36] could be also relevant. For example, Rouse and Willitsch provide evidence in their paper [3] that at absolute temperature $T = 0$ log-normal superstatistics is relevant in ion traps rather than χ^2 superstatistics. For small but finite temperatures T of the buffer gas, however, q-statistics of the type discussed here is in best agreement with the quantum tunneling experiment performed at high

densities. Boltzmann-Gibbs, i.e., the case $q = 1$, then simply describes a noninteracting field theory for entropy, this case is recovered for density $n \to 0$. The experimental validation of these and/or similar features, i.e., systematic measurements of the equation of state $q = q(n)$ and of the temperature fluctuation statistics would be very welcome in future experiments.

Universality of the results. Our theory predicts the existence of fundamental universal temperature fluctuations in a nonequilibrium situation that can be experimentally realized and tested by the latest generation of ion trap experiments. These temperature fluctuations are a fundamental effect and need to be distinguished from imperfections of the measuring device. The predicted function $q(n)$ is experimentally measurable and thus the results of our theory are experimentally testable. Universality kicks in at high densities, where the 4 space-time dimensions essentially fix the 4 degrees of freedom that are relevant for the q-Gaussian velocity distributions at the scale $n_{\max}$. But also at low densities, where quantum tunneling is the dominant effect to enable the chemical reaction, our theory is applicable, as it predicts that in this case the parameter $q - 1$ scales as $n^{2/3}$ if the density n goes to zero.

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[38] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevResearch.7.L012081 for further details on non-additive entropies S_q.