Nonextensive Thermodynamics of a Cluster consisting of $M$ Hubbard Dimers ($M = 1, 2, 3$ and $\infty$) *

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The thermodynamical property of a small cluster including $M$ Hubbard dimers, each of which is described by the two-site Hubbard model, has been discussed within the nonextensive statistics (NES). We have calculated temperature and magnetic-field dependences of the specific heat and susceptibility for $M = 1, 2, 3$ and $\infty$, assuming the relation between $M$ and the entropic index $q$ given by $q = 1 + 1/M$, which was previously derived by several methods. For relating the physical temperature $T$ to the Lagrange multiplier $\beta$, two methods have been adopted: $T = 1/k_B \beta$ in the method A [Tsallis et al. Physica A 261 (1998) 534], and $T = c_q/k_B \beta$ in the method B [Abe et al. Phys. Lett. A 281 (2001) 126], where $k_B$ denotes the Boltzman constant, $c_q = \sum_i p_i^q$, and $p_i$ the probability distribution of the $i$th state. A comparison between the results calculated by the two methods suggests that the method B may be more appropriate than the method A for small-scale systems.

§1. Introduction

In the last several years, much study has been made with the use of nonextensive statistics (NES) which was initiated by Tsallis.¹⁻⁴ Before discussing the NES, let’s recall the basic feature of the Boltzman-Gibbs statistics (BGS) for a system with internal energy $E$ and entropy $S$, which is immersed in a large reservoir with energy $E_0$ and entropy $S_0$. The temperature of the small system $T$ is the same as that of the reservoir $T_0$ where $T = \delta E/\delta S$ and $T_0 = \delta E_0/\delta S_0$. If we consider the number of possible microscopic states of $\Omega(E_0)$ in the reservoir, its entropy is given by $S_0 = k_B \ln \Omega(E_0)$ where $k_B$ denotes the Boltzmann constant. The probability of finding the small system with the energy $E$ is given by $p(E) = \Omega(E_0 - E)/\Omega(E) \sim \exp(-E/k_B T)$ with $E \ll E_0$. When the physical quantity $Q$ of a system containing $N$ particles is expressed by $Q \propto N^\gamma$, it is classified into two groups in the BGS: intensive ($\gamma = 0$) or extensive one ($\gamma = 1$). The temperature and energy are typical intensive and extensive quantities, respectively. This is not the case in the NES, as will be shown below.

In the NES, on the contrary, the temperature of a nanosystem which is in contact with the reservoir, is expected to fluctuate around the temperature of the reservoir $T_0$ because of the smallness of nanosystems and their quasi-thermodynamical equilibrium states with the reservoir. Then the BGS distribution mentioned above has to

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be averaged over the fluctuating temperature. This idea has been expressed by \(^{5)6)7)}\)

\[
p(E) = \int_0^\infty d\beta \ e^{-\beta E} \ f^B(\beta) \nonumber \\
= [1 - (1 - q)\beta_0 E]^{\frac{1}{1-q}} \equiv \exp_q(-\beta_0 E), \tag{1.1}
\]

with

\[
q = 1 + \frac{2}{N}, \tag{1.2}
\]

\[
f^B(\beta) = \frac{1}{\Gamma \left(\frac{N}{2}\right)} \left( \frac{N}{2\beta_0} \right)^{\frac{N}{2} - 1} \exp \left( -\frac{N\beta}{2\beta_0} \right), \tag{1.3}
\]

\[
\beta_0 = \frac{1}{k_B T_0} = \int_0^\infty d\beta f(\beta) \beta \equiv E(\beta), \tag{1.4}
\]

\[
\frac{2}{N} = \frac{E(\beta^2) - E(\beta)^2}{E(\beta)^2}, \tag{1.5}
\]

where \(\exp_q(x)\) denotes the \(q\)-exponential function defined by

\[
\exp_q(x) = [1 + (1 - q)x]^{\frac{1}{1-q}}, \quad \text{for } 1 + (1 - q)x > 0 \\
= 0, \quad \text{otherwise} \tag{1.6}
\]

\(q\) expresses the entropic index, \(E(Q)\) the expectation value of \(Q\) averaged over the \(\Gamma\) (or \(\chi^2\)) distribution function \(f^B(\beta)\), \(\beta_0\) the average of the fluctuating \(\beta\) and \(2/N\) its dispersion. The \(\Gamma\) distribution is emerging from the sum of squares of \(N\) Gaussian random variables, related discussion being given in Sec. 3.

The functional form of the probability distribution \(p(E)\) expressed by Eq. (1.1) was originally derived by the maximum entropy method\(^{1)2)}\) with the generalized entropy given by

\[
S_q = k_B \left( \frac{\sum_i p_i^q - 1}{1 - q} \right) = -k_B \sum_i p_i^q \ln_q(p_i), \tag{1.7}
\]

where \(p_i = p(\epsilon_i)\) denotes the probability distribution for the energy \(\epsilon_i\) in the system, and \(\ln_q(x) = (x^{1-q} - 1)/(1 - q)\) the \(q\)-logarithmic function, the inverse of the \(q\)-exponential function. The important consequence of the NES is that entropy and energy are not proportional to \(N\) in nanosystems.

In our previous papers\(^{8),9)}\) (referred to as I and II, respectively), we have applied the NES to the Hubbard model, which is one of the most important models in solid-state physics. Thermodynamical properties of canonical\(^{8),9)}\) and grand-canonical ensembles\(^9)}\) of a Hubbard dimer described by the two-site Hubbard model have been calculated within the NES. It has been shown that the specific heat and susceptibility calculated by the NES may be significantly different from those calculated by the BGS when the entropic index \(q\) departs from unity, the NES with \(q = 1\) reducing to the BGS.
Nonextensive Thermodynamics of Hubbard dimers

We will consider in the present paper, a nanocluster containing multiple \((M)\) Hubbard dimers in order to discuss the \(M\) dependence of their thermodynamical properties. We have assumed the \(M-q\) relation:

\[
q = 1 + \frac{1}{M}, \quad (1.8)
\]

which is derived from Eq. (1.2) with \(N=2M\).

The paper is organized as follows. After discussing the adopted model and calculation method, we will present in §2, numerical calculations of temperature and magnetic-field dependences of thermodynamical quantities for various \(M\) values. The final §3 is devoted to discussion and conclusion.

§2. Nonextensive statistics for Hubbard dimers

2.1. Adopted model and calculation method

We have adopted canonical ensembles of a small cluster containing \(M\) Hubbard dimers, each of which is described by the two-site Hubbard model. Interdimer interactions are assumed to be negligibly small. The Hamiltonian is given by

\[
H = \sum_{\ell=1}^{M} H^{(d)}_{\ell}, \quad (2.1)
\]

\[
H^{(d)}_{\ell} = -t \sum_{\sigma} (a_{1\sigma}^\dagger a_{2\sigma} + a_{2\sigma}^\dagger a_{1\sigma}) + U \sum_{j=1}^{2} n_{j\uparrow} n_{j\downarrow} - \mu_B B \sum_{j=1}^{2} (n_{j\uparrow} - n_{j\downarrow}),
\]

\[ (1,2 \in \ell) \quad (2.2) \]

where \(H^{(d)}_{\ell}\) denotes the Hamiltonian for the \(\ell\)th dimer, \(n_{j\sigma} = a_{j\sigma}^\dagger a_{j\sigma}\) an annihilation operator of an electron with spin \(\sigma\) on a site \(j\) \((\in \ell)\), \(t\) the hopping integral, \(U\) the intraatomic interaction, \(\mu_B\) the Bohr magneton and \(B\) an applied magnetic field. Six eigenvalues of \(H^{(d)}_{\ell}\) are given by

\[
\epsilon_i = 0, \ 2\mu_B B, \ -2\mu_B B, \ U, \ \frac{U}{2} + \Delta, \ \frac{U}{2} - \Delta, \quad \text{for} \ i = 1 - 6 \quad (2.3)
\]

where \(\Delta = \sqrt{U^2/4 + 4t^2} \) \(10)^{11}\) The number of eigenstates of the total Hamiltonian \(H\) is \(6^M\).

The entropy \(S_q\) in the Tsallis NES is defined by\(^1\)\(^2\)

\[
S_q = k_B \left( \frac{\text{Tr}(\rho_q^2) - 1}{1 - q} \right). \quad (2.4)
\]

Here \(\rho_q\) stands for the generalized canonical density matrix, whose explicit form will be determined shortly [Eq. (2.7)]. We impose the two constraints given by

\[
\text{Tr}(\rho_q) = 1, \quad (2.5)
\]

\[
\frac{\text{Tr}(\rho_q^2 H)}{\text{Tr}(\rho_q^2)} \equiv < H >_q = E_q, \quad (2.6)
\]
where the normalized formalism is adopted.\textsuperscript{2) The variational condition for the entropy with the two constraints given by Eqs. (2.5) and (2.6) yields

$$\rho_q = \frac{1}{X_q} \exp_q \left[ - \left( \frac{\beta}{c_q} \right) (H - E_q) \right], \quad (2.7)$$

with

$$X_q = \text{Tr} \left( \exp_q \left[ - \left( \frac{\beta}{c_q} \right) (H - E_q) \right] \right), \quad (2.8)$$

$$c_q = \text{Tr} (\rho_q^q) = X_q^{1-q}, \quad (2.9)$$

where exp\(_q[x]\) expresses the \(q\)-exponential function defined by Eq. (1.6) and \(\beta\) is a Lagrange multiplier:

$$\beta = \frac{\partial S_q}{\partial E_q}. \quad (2.10)$$

Specific heat and susceptibility have been calculated in I and II.

For relating the physical temperature \(T\) to the Lagrange multiplier \(\beta\), we have adopted the two methods A and B, given by\textsuperscript{9)}

$$T = \frac{1}{k_B \beta}, \quad \text{(method A)} \quad (2.11)$$

$$= \frac{c_q}{k_B \beta}, \quad \text{(method B)} \quad (2.12)$$

The method A proposed in Ref. 2 is the same as the extensive BGS. The method B is introduced so as to satisfy the zeroth law of thermodynamical principles and the generalized Legendre transformations.\textsuperscript{12)} It has been demonstrated that the negative specific heat of a classical gas model which is realized in the method A,\textsuperscript{13)} is remedied in the method B.\textsuperscript{12)} A difference between the two methods does not matter as far as we consider only the non-exponential distribution in the NES. It yields, however, a significant difference in the temperature dependence of thermodynamical quantities, as will be shown in the following subsection.

2.2. Numerical calculations

2.2.1. Temperature dependence

In order to study how thermodynamical quantities of a cluster with Hubbard dimers depend on its size \(M\), we have made numerical calculations, assuming the \(M - q\) relation given by Eq. (1.8), where results for \(M = \infty\) correspond to those of the BGS (\(q = 1\)). Figures 1(a)-1(d) show the results for \(U/t = 5\). The specific heat and susceptibility shown in Figs. 1(a) and 1(b), have been calculated by the method A with \(q = 2.0, 1.5\), and 1.333 for \(M = 1, 2\) and 3, respectively. Figures 1(c) and 1(d) express \(C_q\) and \(\chi_q\), respectively, calculated by the method B. We note that physical quantities in a small cluster with \(M \sim 1 - 3\) are rather different from those of bulk-like systems with \(M = \infty\), although properties of clusters gradually approach those of bulk with increasing \(M\).

We note in Figs. 1(a)-1(d) that by varying \(M\), the maximum values of the specific heat \((C_q^*)\) and the susceptibility \((\chi_q^*)\) and corresponding temperatures of \(T^*_C\)
and \( T_{\chi}^* \) are changed. Figure 2(a) shows \( T_C^* \) and \( T_{\chi}^* \), and Fig. 2(b) depicts \( C_q^* \) and \( \chi_q^* \), which are plotted against \( M^{-1} \): solid and dashed lines denote results calculated by the methods A and B, respectively. It is shown in Fig. 2(a) that with increasing \( M^{-1} \), \( T_{\chi}^* \) calculated by the method A is much increased than that calculated by the method B. We note also that with increasing \( M^{-1} \), \( T_C^* \) of the method B is increased while that of the method A is decreased. Figure 2(b) shows that \( C_q^* \) in the method A is smaller than that in the method B, whereas \( \chi_q^* \) in the method A is the same as that in the method B.

2.2.2. Magnetic-field dependence

From the \( B \) dependence of the six eigenvalues of \( \epsilon_i \) [Eq. (2.3)], we note the crossing of the eigenvalues of \( \epsilon_3 \) and \( \epsilon_6 \) at the critical field:

\[
\mu_B B_c = \sqrt{\frac{U^2}{16} \left( \frac{t^2}{U^2} - 1 \right)},
\]

leading to \( \mu_B B_c/t = 0.351 \) for \( U/t = 5.0 \). For \( B < B_c \) \( (B > B_c) \), \( \epsilon_6 \) \( (\epsilon_3) \) is the ground state. At \( B \sim B_c \) the magnetization \( m_q \) is rapidly increased as shown in Figs. 3(a) and 3(b) for \( k_B T/t = 1.0 \) and 0.1, respectively: the transition at lower temperature is more evident than at higher temperature. This level crossing also yields a peak in \( \chi_q \) [Figs. 3(c) and 3(d)] and a dip in \( C_q \) [Figs. 3(e) and 3(f)]. It is interesting that the peak of \( \chi_q \) for \( q = 1.5 \) in the NES is more significant than that in the BGS whereas that of \( C_q \) of the former is broader than that of the latter. When the temperature becomes higher, these peak structures become less evident. Similar phenomenon in the field-dependent specific heat and susceptibility have been pointed out in the Heisenberg model within the BGS.\(^{14}\)

Figure 3(a) and 3(b) remind us the quantum tunneling of magnetization observed in magnetic molecular clusters such as Mn4, Mn12 and Fe8.\(^{15}\) It originates from the level crossing of magnetic molecules which are parallel and anti-parallel to the easy axis when a magnetic field is applied.

\( \S 3. \) Discussions and conclusions

The \( N - q \) relation given by \( q = 1 + 2/N \) [Eq. (1.2)] has been derived from the average of the BGS partition function over the \( \Gamma \) distribution \( f^B \) given by Eq. (1.3). By using the large-deviation approximation, Touchette\(^{16}\) has obtained the alternative distribution function \( f^T(\beta) \) given by

\[
f^T(\beta) = \frac{\beta_0}{\Gamma \left( \frac{N\beta_0}{2} \right)} \left( \frac{N\beta_0}{2} \right)^{\frac{N}{2} - 1} \beta^{-\frac{N}{2}} \exp \left( -\frac{N\beta_0}{2\beta} \right).
\]

Solid and dashed curves in Fig. 4 express the \( f^B \)- and \( f^T \)-distribution functions, respectively, for various \( N \) values. For \( N \rightarrow \infty \), both reduce to the delta-function densities, and for a large \( N = 100 \), both distribution functions lead to similar results. For a small \( N \) \( (< 10) \), however, there is a clear difference between the two distribution functions. We note that a change of variable \( \beta \rightarrow \beta^{-1} \) in \( f^T \) yields the distribution
function similar to $f^B$. It should be noted that $f^T$ cannot lead to the $q$-exponential function which plays a crucial role in the NES. For a large $\epsilon$, $f^T$ leads to the stretched exponential form of $p(\epsilon) \sim e^{\epsilon / \epsilon^T}$ while $f^B$ yields the power form of $p(\epsilon) \sim \epsilon^{-1} q^{-1}$. This issue of $f^B$ versus $f^T$ is related to the superstatistics, which is currently studied with much interest.\(^{17}\)

Numerical calculations presented in the preceding section have shown that although results calculated by the two methods A and B are qualitatively similar, there are some quantitative difference, as previously obtained in I and II. When we calculate the Curie constant $\Gamma_q$ of the susceptibility defined by $\chi_q(T) = (\mu_B^2 / k_B)[\Gamma_q(T) / T]$, the method A leads to anomalously large Curie constant compared to that of the method B.\(^{9}\) This agrees with the results for free spins\(^9\)\(^{18}\) and for spin dimers described by the Heisenberg model.\(^{22}\) A comparison between Eqs. (1.1) and (2.7) yield the average temperature $< T >$ given by

$$\frac{1}{k_B} < T > \simeq \beta_o = \frac{\beta}{c_q}$$  (3.2)

which is consistent with the method B. These results suggest that the method B is more appropriate than the method A. This is consistent with recent theoretical analyses\(^{19}\)\(^{20}\) [for a relevant discussion, see also Ref. 21].

In summary, within the framework of the NES, thermodynamical properties have been discussed of a cluster including $M$ dimers, each of which is described by the two-site Hubbard model. We have demonstrated that the thermodynamical properties of small-scale systems are rather different from those of bulk systems. Owing to recent progress in atomic engineering, it is possible to synthesize molecules containing relatively small numbers of magnetic atoms with the use of various methods (for reviews, see Refs. 21-23). Theoretical and experimental studies on nanoclusters with changing $M$ could clarify a link between the behavior of the low-dimensional infinite systems and nanoscale finite-size systems. The unsettled issues on $T - \beta$ and the $N - q$ relations in the current NES are expected to be resolved by future theoretical and experimental studies on nanosystems, which are expected to be one of ideal systems for a study on the NES.

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Fig. 1. The temperature dependences of (a) specific heat $C_q$ and (b) susceptibility $\chi_q$ (per dimer) of Hubbard dimers for $U/t = 5$ calculated by the method A, and those of (c) specific heat $C_q$ and (d) susceptibility $\chi_q$ calculated by the method B, with $M = 1$ (bold solid curves), $M = 2$ (chain curves), $M = 3$ (dashed curves) and $M = \infty$ (solid curves).

Fig. 2. (a) $1/M$ dependence of the temperatures of $T_{C}^*$ (circles) and $T_{\chi}^*$ (squares) where $C_q$ and $\chi_q$ have the maximum values, respectively. (b) $1/M$ dependence of the maximum values of $C_{q}^*$ (circles) and $\chi_{q}^*$ (squares). Solid and dashed lines denote the results calculated by the methods A and B, respectively: $T_{\chi}^*$ calculated by the method A shown in (a) is divided by a factor of five.

Fig. 3. The magnetic-field dependence of (a) the magnetization $m_q$ for $k_B T/t = 1.0$ and (b) $k_B T/t = 0.1$, (c) the susceptibility for $k_B T/t = 1.0$ and (d) $k_B T/t = 0.1$, (e) the specific heat $\chi_q$ for $k_B T/t = 1.0$ and (f) $k_B T/t = 0.1$, with $U/t = 5$ for $M = 2$ calculated by the method A (solid curves) and B (dashed curves) and for $M = \infty$ (chain curves).

Fig. 4. The distributions of $f_B(\beta)$ (solid curves) and $f_T(\beta)$ (dashed curves) as a function of $\beta$ (see text).