Nonextensive thermodynamics of the two-site Hubbard model

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Abstract

Thermodynamical properties of canonical and grand-canonical ensembles of the half-filled two-site Hubbard model have been discussed within the framework of the nonextensive statistics (NES). 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 Boltzmann constant, $c_q = \sum_i p_i^q$, $p_i$ the probability distribution of the $i$th state, and $q$ the entropic index. Temperature dependences of specific heat and magnetic susceptibility have been calculated for $1 \leq q \leq 2$, the conventional Boltzmann-Gibbs statistics being recovered in the limit of $q = 1$. The Curie constant $\Gamma_q$ of the susceptibility in the atomic and low-temperature limits ($t/U \to 0$, $T/U \to 0$) is shown to be given by $\Gamma_q = 2q 2^{q-1}$ in the method A, and $\Gamma_q = 2q$ in the method B, where $t$ stands for electron hoppings and $U$ intra-atomic interaction in the Hubbard model. These expressions for $\Gamma_q$ are shown to agree with the results of a free spin model which has been studied also by the NES with the methods A and B. A comparison has been made between the results for canonical and grand-canonical ensembles of the model.

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1 INTRODUCTION

In the last several years, there is an increased interest in the nonextensive statistics (NES), which was initially proposed by Tsallis [1, 2, 3]. This is because the standard method based on the Boltzman-Gibbs statistics (BGS) cannot properly deal with nonextensive systems where the physical quantity associated with $N$ particles is not proportional to $N$ [4]. The nonextensivity has been realized in three different classes of systems: (a) systems with long-range interactions, (b) small-scale systems with fluctuations of temperatures or energy dissipations, and (c) multifractal systems [3, 5]. In a gravitating system with the long-range interaction, which is a typical case (a), the specific heat becomes negative [6]. A cluster of 147 sodium atoms, which belongs to the case (b), has been reported to show the negative specific heat [7]: note that the specific heat is never negative in the canonical BGS [8].

Tsallis [1][2] has proposed a generalized entropy in the NES defined by

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

where $k_B$ denotes the Boltzman constant, $p_i$ the probability distribution of the system in the $i$th configuration, and $q$ the entropic index. The entropy of BGS, $S_{BG}$, is obtained from Eq. (1) in the limit of $q = 1$, as given by

$$S_1 = S_{BG} = -k_B \sum_i p_i \ln p_i. \quad (2)$$

The nonextensivity in the Tsallis entropy is satisfied as follows. Suppose that the total system is divided into two independent subsystems with the probability distributions, $p_i^{(1)}$ and $p_i^{(2)}$. The total system is described by the factorized probability distribution $p_{ij} = p_i^{(1)} p_j^{(2)}$. The entropy for the total system given by Eq. (1) satisfy the relation:

$$S_q = S_q^{(1)} + S_q^{(2)} + \left( \frac{1 - q}{k_B} \right) S_q^{(1)} S_q^{(2)}, \quad (3)$$

where $S_q^{(k)}$ stands for the entropy of the $k$th subsystem. Equation (3) shows that the entropy is extensive for $q = 1$ and nonextensive for $q \neq 1$: the quantity $|q - 1|$ expresses the measure of the nonextensivity. The new formalism has been successfully applied to a wide range of nonextensive systems including physics, chemistry, mathematics, astronomy, geophysics, biology, medicine, economics, engineering, linguistics, and others [5].

The current NES, however, is not complete, having following unsolved issues.
A full and general understanding of the relation between the entropic index $q$ and the underlying microscopic dynamics is lacking. The index $q$ is usually obtained in a phenomenological way by a fitting of experimental or computational available data. It has been reported that the observed velocity distribution of galaxy clusters significantly deviates from BGS distribution, which may be fitted well by the NES distribution with $q \sim 0.23$ [9]. The index $q$ in self-gravitating systems has been shown to be $q = 0.60 \sim 0.92$ for $n = 3 \sim 20$ with the use of the relation: $n = 1/(1 - q) + 1/2$ for the entropic index $q$ and the polytrope index $n$ given by $P(r) \propto \rho(r)^{1+1/n}$, where $P(r)$ is pressure and $\rho(r)$ mass density [10]. However, the index $q$ has been successfully determined a priori in some cases [3]. In one-dimensional dissipative map, the index is given by $q = 0.2445$ [11] from its scaling property of dynamic attractors. In nanometric systems consisting of $N$ noninteracting particles, the NES distribution is shown to arise from fluctuating $\beta$ whose distribution is given by the $\chi^2$ (or $\Gamma$) distribution, leading to $q = 1 + 2/N$ [12, 13, 14].

(ii) The second issue is that it is not clear how to relate the physical temperature $T$ to the introduced Lagrange multiplier $\beta$. So far two methods have been proposed:

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

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

where $c_q = \sum_i p_i^q$. 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 [15]. It has been demonstrated that the negative specific heat of a classical gas model which is realized in the method A [16], is remedied in the method B [15]. Results calculated with the use of the two methods have been compared in self-gravitating systems [17].

In this paper, we wish to apply the NES to the Hubbard model, which is one of the most important models in condensed-matter physics (for a recent review on the Hubbard model, see Ref.[18]). The Hubbard model consists of the tight-binding term expressing electron hoppings and the short-range interaction between two electrons with opposite spins. The model provides us with good qualitative description for many interesting phenomena such as magnetism, electron correlation, and superconductivity. In particular, the model has been widely employed for a study of metallic magnetism. In the atomic limit where the electron interaction is much larger than electron hoppings, the Hubbard model with the half-filled band reduces to a local-spin model such as the Heisenberg and Ising models. Despite the simplicity of the Hubbard, however, it is very difficult to obtain...
its exact solution. In order to get a reasonable solution, various technical methods have been developed [18]. It is possible to employ a small number of lattice models to obtain an analytical solution. The two-site Hubbard model is employed as a simple model which can be analytically solved. Thermodynamical and magnetic properties of the two-site model have been studied within the BGS [19, 20, 21]. Although the two-site Hubbard model is a toy model, it is an exactly solvable quantum system. Actually this model may be adopted to describe interesting phenomena in real systems such as organic charge-transfer salts with dimerized structures [19]-[22]. Because the two-site Hubbard model is considered to belong to the case (b) of small-scale systems mentioned above, it is worthwhile to apply the NES to the model in order to investigate nonextensive effects on its thermodynamical and magnetic properties, which is the purpose of the present paper.

The paper is organized as follows. After discussing the NES for grand-canonical ensembles (GCE) of the two-site Hubbard model in Sec. 2, we will calculate the specific heat, susceptibility and the Curie constant of the susceptibility in the atomic limit calculated by the NES with the two methods A and B for the $T - \beta$ relations given by Eqs. (4) and (5). In Sec. 3, we present calculations for canonical ensembles (CE) of the model, which are compared to those for GCE. The final Sec. 4 is devoted to discussions and conclusions. In appendix A, free spin systems have been discussed also by using the NES with the two methods A and B.

2 Grand-canonical ensembles

2.1 Entropy, energy and free energy

We consider GCE of the half-filled, two-site Hubbard model given by

$$\hat{H} = -t \sum_\sigma (a_{1\sigma}^\dagger a_{2\sigma} + a_{2\sigma}^\dagger a_{1\sigma}) + U \sum_{j=1}^2 n_{j\uparrow} n_{j\downarrow} - h \sum_{j=1}^2 (n_{j\uparrow} - n_{j\downarrow}),$$

(6)

where $n_{j\sigma} = a_{j\sigma}^\dagger a_{j\sigma}$, $a_{j\sigma}$ denotes the annihilation operator of an electron with spin $\sigma$ on a site $j$ ($=1, 2$), $t$ the hopping integral, $U$ the intraatomic interaction and $h$ an applied magnetic field in an appropriate unit. Eigen values of the system are given by [21]

$$\epsilon_i = \begin{cases} 0, & \text{for } i = 1 \ (n_i = 0) \\ \pm t \pm h, & \text{for } i = 2 \text{ to } 5 \ (n_i = 1) \\ 0, \pm 2h, U, U/2 \pm \Delta, & \text{for } i = 6 \text{ to } 11 \ (n_i = 2) \end{cases}$$

(7)
\[ U \pm t \pm h, \quad \text{for } i = 12 \text{ to } 15 \quad (n_i = 3) \quad (10) \]

\[ 2U, \quad \text{for } i = 16 \quad (n_i = 4) \quad (11) \]

where \( \Delta = \sqrt{U^2/4 + 4t^2} \), and \( n_i \) expresses the number of electrons in the \( i \)th state. The grand-partition function in BGS, \( \Xi_{BG} \), is given by \((k_B = 1 \text{ hereafter})\) \[21\]

\[ \Xi_{BG} = Tr e^{-(\hat{H} - \mu \hat{N})/T}, \quad (12) \]

\[ = 1 + 4 \cosh(h/T) \cosh(t/T) \] \[ e^{\mu/T} \]

\[ + [1 + 2 \cosh(2h/T) + e^{-U/T} + 2 e^{-U/2T} \cosh(\Delta/T)] e^{2\mu/T} \]

\[ + 4 \cosh(h/T) \cosh(t/T) \] \[ e^{-(U-3\mu)/T} + e^{-2(U-2\mu)/T}. \quad (13) \]

Here \( Tr \) stands for trace, \( \hat{N} = \sum_{i=1}^{2} \sum_{\sigma} n_{i\sigma} \), and the chemical potential is \( \mu = U/2 \) independent of the temperature in the half-filled case where the number of total electrons is \( N_e = 2 \). By using the standard method in the BGS, we can obtain various thermodynamical quantities of the system \([21]\).

Now we adopt the NES in which the entropy \( S_q \) is given by \([1][2]\)

\[ S_q = \left( \frac{Tr (\hat{\rho}_q) - 1}{1 - q} \right). \quad (14) \]

Here \( \hat{\rho}_q \) denotes the generalized density matrix, whose explicit form will be determined shortly \([\text{Eq. (18)}]\). We impose the three constraints given by

\[ Tr (\hat{\rho}_q) = 1, \quad (15) \]

\[ \frac{Tr (\hat{\rho}_q \hat{H})}{Tr (\hat{\rho}_q)} \equiv < \hat{H} >_q = E_q, \quad (16) \]

\[ \frac{Tr (\hat{\rho}_q \hat{N})}{Tr (\hat{\rho}_q)} \equiv < \hat{N} >_q = N_q, \quad (17) \]

where the normalized formalism is adopted \([2]\). The variational condition for the entropy with the three constraints given by Eqs. \((15)-(17)\) yields

\[ \hat{\rho}_q = \frac{1}{X_q} \exp_q \left[ - \left( \frac{\beta}{c_q} \right) \left( \hat{H} - \mu \hat{N} - E_q + \mu N_q \right) \right], \quad (18) \]

with

\[ X_q = Tr \left( \exp_q \left[ - \left( \frac{\beta}{c_q} \right) (\hat{H} - \mu \hat{N} - E_q + \mu N_q) \right] \right), \quad (19) \]

\[ c_q = Tr (\hat{\rho}_q) = X_q^{1-q}, \quad (20) \]
where \( \exp_q(x) \equiv [1 + (1 - q)x]^{\frac{1}{1-q}} \) is the generalized exponential function. Lagrange multipliers \( \beta \) and \( \mu \) relevant to the constraints given by Eqs. (16) and (17) are given by the relations:

\[
\beta = \frac{\partial S_q}{\partial E_q}, \\
\mu = -\frac{1}{\beta} \frac{\partial S_q}{\partial N_q}.
\]  

The entropy \( S_q \) in Eq. (14) is expressed by

\[
S_q = \left( \frac{X_q^{1-q} - 1}{1-q} \right) \equiv \ln_q \left( X_q \right),
\]

where \( \ln_q(x) \equiv (x^{1-q} - 1)/(1-q) \) is the generalized logarithmic function.

In relating the physical temperature \( T \) to the Lagrange multiplier \( \beta \), we have adopted the two methods [2][15]:

\[
T = \frac{1}{\beta}, \quad \text{(method A)} \tag{24}
\]

\[
= \frac{c_q}{\beta}, \quad \text{(method B)} \tag{25}
\]

In the limit of \( q = 1 \), we get the results obtained in the BGS: \( \hat{\rho}_{BG} = e^{-\beta(\hat{H}-\mu\hat{N})}/\Xi_{BG} \), \( E_{BG} = Tr(\hat{\rho}_{BG}\hat{H}) \), \( N_{BG} = Tr(\hat{\rho}_{BG}\hat{N}) \), \( X_{BG} = e^{\beta(E_{BG}-\mu N_{BG})}/\Xi_{BG} \), \( \Xi_{BG} = Tr(e^{-\beta(\hat{H}-\mu\hat{N})}) \), and \( S_{BG} = -Tr(\ln \hat{\rho}_{BG}) \).

It is necessary to point out that \( E_q \) and \( X_q \) have to be determined self-consistently by Eqs. (16)-(20) with \( \mu \) determined by Eq. (22) for \( N_q = N_e \) and a given temperature \( T \) because they are mutually dependent. In the half-filled case, however, calculations become easier because \( \mu = U/2 \) independent of the temperature. The calculation of thermodynamical quantities in the NES generally becomes more difficult than that in BGS. In our numerical calculations to be reported in this paper, simultaneous equations for \( E_q \) and \( X_q \) given by Eqs. (16)-(20) are solved by using the Newton-Raphson method. The iteration have started with initial values of \( E_q \) and \( X_q \) obtained from the BGS (\( q = 1 \)). Numerical calculations have been made for \( 1 \leq q \leq 2 \) which is appropriate for nanoscale systems[12, 13, 14].

Figures 1(a)-1(f) show the temperature dependence of the energy \( E_q \) of GCE calculated for \( \hbar = 0 \). Bold solid curves in Fig. 1(a), 1(b) and 1(c) show \( E_1 \) in the BGS calculated for \( U/t = 0, 5 \) and 10, respectively. The ground-state energy at \( T = 0 \) is \( E_1/t = -2.0, -0.70156 \) and -0.38516 for \( U/t = 0, 5 \) and 10, respectively. With increasing \( q \) value above
unity, the gradient of $E_q$ is much decreased in the method A, as shown in Figs. 1(a)-1(c). This trend is, however, much reduced in the method B, as Figs. 1(d)-1(f) show. This behavior is more clearly seen in the temperature dependence of the specific heat $C_q$, as will be discussed shortly [Figs. 3(a)-3(f)].

Temperature dependences of the entropy for $h = 0$ are plotted in Figs. 2(a)-2(f). Figures 2(a), 2(b) and 2(c) express $S_q$ for $U/t = 0$, 5 and 10, respectively, calculated by the method A, and Figs. 2(d)-2(f) those calculated by the method B. Bold curves denote the results for the BGS, where the entropy is quickly increased at low temperature when the interaction is increased. When the $q$ value is more increased above unity, $S_q$ is more rapidly increased at very low temperatures and its saturation value at higher temperatures becomes smaller. This behavior is commonly realized in the results calculated by the methods A and B. A difference between the two results is ostensibly small because $S_q$ shows a saturation at low temperatures.

### 2.2 Specific heat

First we consider the specific heat, which is given by

$$C_q = \left( \frac{d\beta}{dT} \right) \left( \frac{dE_q}{d\beta} \right).$$

(26)

Because $E_q$ and $X_q$ are determined by Eqs. (16)-(20), we get simultaneous equations for $dE_q/d\beta$ and $dX_q/d\beta$, given by

$$\frac{dE_q}{d\beta} = a_{11} \left( \frac{dE_q}{d\beta} \right) + a_{12} \left( \frac{dX_q}{d\beta} \right) + b_1,$$

(27)

$$\frac{dX_q}{d\beta} = a_{21} \left( \frac{dE_q}{d\beta} \right) + a_{22} \left( \frac{dX_q}{d\beta} \right),$$

(28)

with

$$a_{11} = q\beta X^q \sum_i w_i^{2q-1} \epsilon_i,$$

(29)

$$a_{12} = -X^{-1} E_q - \beta q(q - 1) X^{-3} \sum_i w_i^{2q-1} \epsilon_i (\epsilon_i - \mu n_i - E_q + \mu N_e),$$

(30)

$$a_{21} = \beta X^q,$$

(31)

$$a_{22} = 0,$$

(32)

$$b_1 = -qX^{-2} \sum_i w_i^{2q-1} \epsilon_i (\epsilon_i - E_q),$$

(33)

$$w_i = \langle i | \exp \left[ - \left( \frac{\beta}{c_q} \right) (H - \mu N - E_q + \mu N_e) \right] | i \rangle,$$
\[ X_q = \sum_i w_i. \]  

(35)

The specific heat is then given by

\[ C_q = \left( \frac{d\beta}{dT} \right) \left( \frac{b_1}{1 - a_{11} - a_{12}a_{21}} \right). \]  

(36)

with

\[ \frac{\partial \beta}{\partial T} = -\beta^2, \]  

(method A) \hspace{1cm} (37)

\[ \frac{\partial \beta}{\partial T} = -\left( \frac{\beta^2}{X_q^{1-q} - \beta(1-q)X_q^{-q}(dX_q/d\beta)} \right), \]  

(method B) \hspace{1cm} (38)

\[ \frac{dE_q}{d\beta} = \frac{b_1}{(1 - a_{11} - a_{12}a_{21})}, \]  

(39)

\[ \frac{dX_q}{d\beta} = \frac{a_{21}b_1}{(1 - a_{11} - a_{12}a_{21})}, \]  

(40)

It is worthwhile to examine the limit of \( q = 1 \) of Eqs.(29)-(35), which reduce to

\[ a_{11} = \beta E_1, \]  

(41)

\[ a_{12} = -X_1^{-1}E_1, \]  

(42)

\[ a_{21} = \beta X_1, \]  

(43)

\[ b_1 = -<\epsilon_i^2>_1 + <\epsilon_i>_1^2. \]  

(44)

yielding

\[ C_1 = \beta^2(<\epsilon_i^2>_1 - <\epsilon_i>_1^2), \]  

(45)

with

\[ <Q_i>_1 = X_1^{-1} \sum_i e^{-\beta(\epsilon_i - \mu n_i - E_1 + \mu N_e)}/Q_i, \]  

(46)

\[ E_1 = <\epsilon_i>_1, \]  

(47)

\[ X_1 = \sum_i e^{-\beta(\epsilon_i - \mu n_i - E_1 + \mu N_e)}. \]  

(48)

The expression for \( C_1 \) agrees with \( C_{BG} \) obtained in the BGS.

Figures 3(a)-3(f) show the specific heat of GCE calculated for \( h = 0 \). \( C_1 \) in BGS for \( U/t = 0 \) shown by the bold solid curve in Fig. 3(a), has a peak at \( T/t \sim 0.65 \).

Figure 3(c) shows that for \( U/t = 10 \), this peak splits into two. A lower peak arises.
from low-lying collective spin-wave-like excitations while higher one from single-particle excitations [20][21]. For intermediate $U/t = 5$ these two peaks overlap [Fig. 3(b)]. The temperature dependences of the specific heat $C_q$ calculated with the use of the method A for $U/t = 0, 5$ and 10 are plotted in Figs. 3(a), 3(b) and 3(c), respectively. We note that when $q$ is larger than unity, peaks become broader. Figures 3(d), 3(e) and 3(f) show the temperatures dependence of the specific heat $C_q$ calculated by the method B for $U/t = 0, 5$ and 10, respectively. Although general property of the $q$ dependence of the specific heat of the method B is similar to that of the method A, the effect of the nonextensivity in the method B becomes smaller than that in the method A.

2.3 Susceptibility

In the NES, the magnetization induced by an applied field $h$ is obtained by

$$m_q = <\mu_i>_q,$$  \hspace{1cm} (49)

leading to the susceptibility given by

$$\chi_q = \frac{\partial m_q}{\partial h} \big|_{h=0},$$  \hspace{1cm} (50)

$$= -E_q^{(2)} + \beta^{-1}X_q^{-q}X_q^{(2)},$$  \hspace{1cm} (51)

where $\mu_i = -\partial \epsilon_i / \partial h$ and $E_q^{(2)} = \partial^2 E_q / \partial h^2 \big|_{h=0}$ et al. With calculations using Eqs. (16)-(20), we get simultaneous equations for $E_q^{(2)}$ and $X_q^{(2)}$, given by

$$E_q^{(2)} = a_{11}E_q^{(2)} + a_{12}X_q^{(2)} + f_1,$$  \hspace{1cm} (52)

$$X_q^{(2)} = a_{21}E_q^{(2)} + a_{22}X_q^{(2)} + f_2,$$  \hspace{1cm} (53)

with

$$f_1 = -2\beta q X_q^{q-2}\sum_i w_i^{2q-1}\mu_i^2,$$  \hspace{1cm} (54)

$$f_2 = \beta^2 q X_q^{2(q-1)}\sum_i w_i^{2q-1}\mu_i^2,$$  \hspace{1cm} (55)

where $a_{ij} (i, j = 1, 2)$ are given by Eqs. (29)-(31). The susceptibilities $\chi_q$ in the methods A and B are expressed by

$$\chi_q = \left(\frac{-a_{12} + \beta^{-1}X_q^{-q}(1 - a_{11})}{1 - a_{11} - a_{12}a_{21}}\right) f_2 = \frac{f_2}{a_{21}},$$  \hspace{1cm} (56)

with the $T - \beta$ relations given by Eqs. (24) and (25), respectively.
In the limit of $q = 1$, Eqs. (54) and (55) reduce to

\begin{align*}
  f_1 &= -2 \beta \langle \mu_i^2 \rangle_1, \quad (57) \\
  f_2 &= \beta^2 X_1 \langle \mu_i^2 \rangle_1, \quad (58)
\end{align*}

leading to the susceptibility in the BGS:

\[ \chi_{BG} = \chi_1 = \beta \langle \mu_i^2 \rangle_1, \quad (59) \]

where the bracket $< \cdot >_1$ is given by Eq. (46).

The BGS susceptibility for $U/t = 0$ has a peak at $T/t \sim 0.65$ as Fig. 4(a) shows. With increasing $U/t$, the magnitude of $\chi_{BG}$ is enhanced by the interaction, and its peak position becomes lower \cite{20,21}, as Figs. 4(b) and 4(c) show: the horizontal scale of Fig. 4(c) is enlarged compared with Figs. 4(a) and 4(b). The temperature dependences of the susceptibility $\chi_q$ calculated by the method A for $U/t = 0$, 5 and 10 are plotted in Figs. 4(a), 4(b) and 4(c), respectively. We note that as increasing $q$ above unity, the peak in $\chi_q$ becomes broader. Figures 4(d), 4(e) and 4(f) show the temperature dependence of the susceptibility $\chi_q$ calculated by the method B for $U/t = 0$, 5 and 10, respectively. Again the effect of the nonextensivity in the method B becomes smaller than that in the method A.

### 2.4 Curie constant in the atomic limit

The half-filled Hubbard model with $t/U \ll 1$ reduces to a local-spin model with the superexchange interaction $J \sim t^2/U$. In the limit of $t/U \to 0$ (atomic limit) for which $J \to 0$, the susceptibility of the two-site Hubbard model in BGS is given by

\begin{align*}
  \chi_{BG} &= \frac{2}{T(1 + e^{-U/2T})}, \\
  &= \frac{2}{T}, \quad \text{for } T \ll U \quad (61) \\
  &= \frac{1}{T}, \quad \text{for } T \gg U \quad (62)
\end{align*}

Defining the effective, temperature-dependent Curie constant $\Gamma_q(T)$ by

\[ \Gamma_q(T) = T \chi_q(T), \quad (63) \]

we note from Eqs. (61) and (62) that it varies from $\Gamma_1(0) = 2$ for localized moments to $\Gamma_1(\infty) = 1$ for delocalized moments.
By using the NES, we get the Curie constant of our model in the low-temperature limit \((T \ll U)\), given by

\[
\Gamma_q(0) = 2qM^{q-1} = 2q2^{2(q-1)}, \quad \text{(method A)} \tag{64}
\]

\[
= 2q, \quad \text{(method B)} \tag{65}
\]

with

\[
X_q = M = 2^2, \tag{66}
\]

where \(M\) denotes the number of states with the lowest value of \(\epsilon_i - \mu\). Similarly, the Curie constant in the high-temperature limit \((T \gg U)\) is given by

\[
\Gamma_q(\infty) = qM^{q-1} = q4^{2(q-1)}, \quad \text{(method A)} \tag{67}
\]

\[
= q, \quad \text{(method B)} \tag{68}
\]

with

\[
X_q = M_{\infty} = 4^2, \tag{69}
\]

where \(M_{\infty}\) expresses the number of available states in our model. Expressions given by Eqs. (64) and (65) are consistent with the results for free spin systems calculated by NES with the methods A and B [Eqs. (90) and (91)], whose detail is discussed in appendix A.

Solid curves in Fig. 5(a) and 5(b) show the temperature dependence of the inversed susceptibility \(1/\chi_q\) for \(t = 0\) with various \(q\) values calculated by the methods A and B, respectively. We notice that as increasing the \(q\) value, the gradient of \(1/\chi_q\) is decreased in both the methods. Solid curves in Fig. 5(c) and 5(d) express the temperature dependence of \(\Gamma_q\) calculated by the methods A and B, respectively. We note that \(\Gamma_1\) is 2 at \(T/U \sim 0\) and approaches 1 at \(T/U \sim 10\), as Eqs. (61) and (62) show. \(\Gamma_2(T)\) in the method A is 16 at \(T/U \sim 0\) and it is rapidly increased as increasing the temperature with the maximum at \(T/U \sim 4\), above which it is decreased. In contrast, \(\Gamma_2(T)\) in the method B starts from 4 at \(T/U \sim 0\), and approaches 2 at \(T/U = 10\) with a peak at \(T/U \sim 0.2\).

We note that in Figs. 5(a)-5(d) that the Curie constant is increased with increasing \(q\). This is more clearly seen in Figs. 5(e) and 5(f), where we plot the \(q\) dependences of \(\Gamma_q(T)\) calculated by the methods A and B, respectively. Circles in Fig. 5(e) show \(\Gamma_q(T)\) at \(T = 0.02\) calculated by the method A, which nicely obeys the relation \(\Gamma_q(0) = 2q2^{2(q-1)}\) [Eq. (64)].

On the contrary, \(\Gamma_q(\infty)\) in the model A is expressed by squares in Fig. 5(e) where the chain curve denotes \(\Gamma_q(\infty) = q4^{2(q-1)}\) [Eq. (67)]. A disagreement between the chain
curve and the result of $T/U = 10$ arises from a fact that the temperature of $T/U = 10$ does not correspond the high-temperature limit, which is realized at $T/U > 100$. Circles in Figure 5(f) show the $q$ dependence of $\Gamma_q(T)$ at $T/U = 0.02$ calculated by the method A, which follows the relation $\Gamma_q(0) = 2q$ given by Eq. (65). On the contrary, $\Gamma_q(T)$ at $T/U = 10$ calculated by the method B is plotted by squares in Fig. 5(f), approximately following the chain curve given by $\Gamma_q(\infty) = q$ [Eq. (68)].

3 Canonical ensembles

In the previous section, we have discussed thermodynamical properties of GCE of the two-site Hubbard model. It is straightforward to extend our study to CE of the model. The canonical partition function $Z_{BG}$ in the BGS is given by [19]

$$Z_{BG} = 1 + 2 \cosh(2h/T) + \frac{e^{-U/T}}{2} \cosh(\Delta/T).$$

(70)

The generalized density matrix $\hat{\rho}_q$ for CE in the NES may be determined by the variational condition for the entropy given by Eq. (14) with the two constraints given by Eqs. (15) and (16) [23]:

$$\hat{\rho}_q = \frac{1}{X_q} \exp_q \left[ -\left( \frac{\beta}{c_q} \right)(\hat{H} - E_q) \right],$$

(71)

with

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

(72)

$$c_q = \text{Tr} (\hat{\rho}_q^q) = X_q^{1-q},$$

(73)

where $\beta$ stands for the Lagrange multiplier and $E_q$ is given by Eq. (16). The $T - \beta$ relations in the methods A and B are given by Eqs. (24) and (25), respectively. The specific heat is expressed by Eqs. (29)-(40) but with $a_{12}$, $w_i$ and $X_q$ given by [23]

$$a_{12} = -X_q^{-1}E_q - \beta q(q-1)X_q^{-3} \sum_i w_i^{2q-1} \epsilon_i(\epsilon_i - E_q),$$

(74)

$$w_i = \left[ 1 - (1-q) \left( \frac{\beta}{c_q} \right)(\epsilon_i - E_q) \right]^{\frac{1}{1-q}},$$

(75)

$$X_q = \sum_i w_i,$$

(76)

where a sum over $i$ ($= 6$ to 11) is only for $n_i = 2$ in Eq. (9). The susceptibility is similarly expressed by Eqs. (54)-(56) with $a_{12}$, $w_i$ and $X_q$ given above. The Curie constants with
$t/U = 0$ in the low-temperature limit are given by Eqs. (64) and (65) in the methods A and B, respectively, while those in the high-temperature limit are given by Eqs. (67) and (68) but with $q \rightarrow (4/3)q$ and $M_\infty = C_2^4$ where $C_k^n = n!/(k!(n-k)!)$.

Temperature dependences of the specific heat $C_q$ of CE calculated for $h = 0$ are plotted in Figs. 6(a)-6(f). Bold curves in Figs. 6(a)-6(c) show the temperature dependence of $C_{BG}$ in the BGS. For $U/t = 0$, $C_{BG}$ calculated for CE is similar to that for GCE shown in Fig. 3(a). For $U/t = 10$, however, the result for CE is rather different from that for GCE shown in Fig. 3(c): the latter has a broad peak at $T/t > 1$ while the former not. The high-temperature peak in $C_{BG}$ of GCE is responsible to charge fluctuations whose effect is included in the GCE treatment but not in the CE one. The temperature dependences of the specific heat in the NES calculated by the method A are plotted in Figs. 6(a)-6(c), whereas those calculated by the method B are shown in Figs. 5(d)-5(f).

Figures 7(a)-7(c) show the temperature dependence of the susceptibility in the NES calculated by the method A. Results calculated by the method B are plotted in Figs. 7(d)-7(f). The difference between the results of CE and GCE is small. This is because the susceptibility is not sensitive to charge fluctuations. Effects of the nonextensivity on $C_q$ and $\chi_q$ in the method B become smaller than those in the method A for CE, just as for GCE.

Although results calculated for CE and GCE coincide for infinite systems, it is not the case for finite ones. The CE-method is appropriate for an analysis of real nanoscale materials where the number of total electrons is conserved. In contrast, the GCE-method is expected to be better in guessing properties of infinite systems from results of finite systems [20]. This is understood as follows. Suppose that an infinite system is divided into many segments. Charge fluctuations exist between adjacent segments, which are taken into account in the GCE statistics.

4 Discussions and Conclusions

Recent progress in atomic engineering makes it possible to create nanoscale materials with the use of various methods (for reviews, see Ref. [24]). Nanomagnetism shows interesting properties different from bulk magnetism. Nanoclusters consisting of transition metals such as Fe$_N$ ($N=15-650$) [25], Co$_N$ ($N=20-200$) [26], and Ni$_N$ ($N=5-740$) [27] have been synthesized by laser vaporization and their magnetic properties have been measured, where $N$ denotes the number of atoms per cluster. Magnitudes of magnetic
moments are increased with reducing $N$ [27]. It is shown that magnetic moments in Co monatomic chains constructed on Pt substrates are larger than those in monolayer Co and bulk Co [28]. Recently Au nanoparticles with average diameter of 1.9 nm (including 212 atoms), which are protected by polyallyl amine hydrochloride (PAAHC), are reported to show ferromagnetism while bulk Au is diamagnetic [29]. This is similar to the case of gas-evaporated Pd fine particles with the average diameter of 11.5 nm which show the ferromagnetism whereas bulk Pd is paramagnetic [30].

The magnetic property of 4 Ni atoms with the tetrahedral structure in magnetic molecules of metallo-organic substance \([\text{Mo}_{12}\text{O}_{30}(\mu_2 - \text{OH})_{10}\text{H}_2\{\text{Ni(H}_2\text{O}_3)\}_4] \cdot 14\text{H}_2\text{O}\) has been studied [31]. Their temperature-dependent susceptibility and magnetization process have been analyzed by using the Heisenberg model with the antiferromagnetic exchange couplings between Ni atoms [31]. Similar analysis has been made for six-, eight-, ten- and twelve-membered Fe atoms in a family of magnetic molecules [32].

It is well known that the Hubbard model is more suitable for a study on bulk magnetism of transition metals than the Heisenberg or Ising model which is best applied to rare-earth-metal magnets like Gd [18]. This is true also for transition-metal nanomagnetism. It is interesting to make a comparison of our result obtained for the two-site Hubbard model with experimental data of nanoclusters consisting of two transition-metal atoms. Our NES calculations have shown that the results for $q = 2$, which is realized for a two-atom molecule if we assume $q = 1 + 2/N$ [12, 13, 14], are rather different from those for $q = 1$ (BGS).

For a better understanding of nanomagnetism, we are requested to perform NES calculations of the $N$-site Hubbard model with a larger $N$ in one, two and three dimensions. The number of eigen values is $4^N$ for the GCE and $C_N^{2N}$ for the CE with the half-filled electron occupancy. When the orbital degeneracy is taken into account for a more realistic description, these numbers become $4^{ND}$ and $C_N^{2ND}$ for GCE and CE, respectively, where $D (= 2L + 1)$ denotes the orbital degeneracy for the orbital quantum number $L$ ($L = 2$
for 3d transition metals) [34]. Realistic NES calculations for larger nanosystems become much laborious. We hope that by extending the current engineering technique, it would be possible to synthesize ideal, small nanoclusters consisting of transition-metal atoms.

To summarize, we have discussed thermodynamical and magnetic properties of GCE and CE of the two-site Hubbard model within the framework of the NES. This is the first application of NES to thermodynamical and magnetic properties of the Hubbard model, as far as the author is aware of. The temperature dependences of the specific heat and susceptibility calculated by the two methods A and B for $T - \beta$ relation, are qualitatively the same, and they change significantly when $q$ deviates from unity. The two methods, however, yield a quite different $q$ dependence of the Curie constant, which is demonstrated for the atomic-limit case, and which is consistent with the result for free spin models as discussed in appendix A. Although the result of the method B is considered to be more reasonable than that of the method A, we reserve to conclude which of the two methods is correct for the two-site Hubbard model at this stage. It is necessary to further develop the NES theory in order to clarify the two issues (i) and (ii) raised in the introduction.

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Appendix A NES for a free spin model

We consider Hamiltonian expressing the $N$ Ising spins with $S = 1/2$, given by

$$ H = -g \hbar \sum_{j=1}^{N} S_{zj} \equiv -g \hbar S_z, $$

where $g(= 2)$ denotes the $g$ factor and $h$ an applied magnetic field in an appropriate units. Eigen states are classified by $m_s = S_z$, which runs from $-N/2$ to $N/2$. The multiplicity of the state specified by $m_s$ is given by [35]

$$ f(m_s, N) = \frac{N!}{(N/2 + m_s)! \ (N/2 - m_s)!}, $$

which satisfies the sum rule:

$$ \sum_{m_s=-N/2}^{N/2} f(m_s, N) = 2^N \equiv M. $$
Hereafter we specify the state with the index \( i \), which runs from 1 to \( M \). In the case of \( N = 2 \), for example, we get \( m_i = -1 \) for \( i = 1 \), \( m_i = 0 \) for \( i = 2, 3 \) and \( m_i = 1 \) for \( i = 4 \).

By employing the NES for CE as in Sec. 3, we get the probability density given by

\[
\begin{align*}
p_i &= \frac{w_i}{X_q}, \\
X_q &= \sum_i w_i, \\
w_i &= \exp_q \left[ \frac{\beta}{c_q} (h m_i + E_q) \right], \\
c_q &= \sum_i p_i^q = X_q^{1-q}, \\
E_q &= X_q^{-1} \sum_i h m_i \left( \exp_q \left[ \frac{\beta}{c_q} (h m_i + E_q) \right] \right)^q,
\end{align*}
\]

The thermal average of the magnetization is given by

\[
m_q = g \left( \frac{\sum_i p_i^q m_i}{\sum_i p_i^q} \right),
\]

from which we get the susceptibility given by

\[
\chi_q = \frac{\partial m_q}{\partial h} \bigg|_{h=0},
\]

\[
= g^2 \left( \frac{q \beta}{X_q^{1-q}} \right) \frac{1}{X_q} \sum_i w_i^{2q-1} m_i^2,
\]

\[
= \frac{N q \beta}{c_q}.
\]

In deriving Eq. (88), we have adopted \( w_i = 1 \) and \( X_q = 2^N \), and

\[
2^{-N} \sum_{m_s=-N/2}^{N/2} f(m_s, N) m_s^2 = \frac{N}{4},
\]

for \( (\beta/c_q)(h m_i + E_q) \ll 1 \) with \( h \to 0 \). When we adopt the method A given by \( T = 1/\beta \) [Eq. (24)], Eq. (88) becomes

\[
\chi_q = \frac{\Gamma_q}{T},
\]

with the Curie constant \( \Gamma_q \) given by

\[
\Gamma_q = N q M^{q-1} = N q 2^{N(q-1)},
\]

which agrees with the result of Ref. [36] previously obtained by using the Tsallis’ normalized scheme [2]. Equation (91) has an anomalous exponential dependence on \( N \), and
shows dark magnetism: the apparent number of spins is larger than the actual one [36, 37]. On the contrary, when we adopt the method B given by $T = c_q/\beta$ [Eq. (25)], the Curie constant becomes

$$\Gamma_q = N q, \quad (92)$$

whose $N$ dependence seems reasonable.

By using the $T - \beta$ relation given by

$$\frac{1}{T} = \frac{\beta}{c_q + (1 - q)\beta E_q}, \quad (93)$$

Reis et al. [35] have obtained the result same as Eq. (91). This is due to a fact that with $E_q = 0$ for $h = 0$, Eq. (92) reduces to $T = c_q/\beta$ which is nothing but the $T - \beta$ relation in the method B.

When we adopt the relation: $q = 1 + 2/N$ obtained for nanoscale systems [12, 13, 14], Eqs. (90) and (91) become

$$\Gamma_q = 4N \left(1 + \frac{2}{N}\right), \quad \text{(method A)} \quad (94)$$

$$= N \left(1 + \frac{2}{N}\right), \quad \text{(method B)} \quad (95)$$

Equation (94) is consistent with the result of the Ising model with $N \to \infty$. 

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Figure 1: The temperature dependences of the energy $E_q$ of grand-canonical ensembles for $h = 0$ with (a) $U/t = 0$, (b) 5 and (c) 10 calculated by the method A (GCE-A), and those with (d) $U/t = 0$, (e) 5 and (f) 10 calculated by the method B (GCE-B): $q = 1.0$ (bold solid curves), 1.1 (dotted curves), 1.2 (dashed curves), 1.5 (chain curves) and 2.0 (solid curves).

Figure 2: The temperature dependences of the entropy $S_q$ of grand-canonical ensembles for $h = 0$ with (a) $U/t = 0$, (b) 5 and (c) 10 calculated by the method A (GCE-A) for $h = 0$, and those with (d) $U/t = 0$, (e) 5 and (f) 10 calculated by the method B (GCE-B): $q = 1.0$ (bold solid curves), 1.1 (dotted curves), 1.2 (dashed curves), 1.5 (chain curves) and 2.0 (solid curves).

Figure 3: The temperature dependences of the specific heat $C_q$ of grand-canonical ensembles for $h = 0$ with (a) $U/t = 0$, (b) 5 and (c) 10 calculated by the method A (GCE-A), and those with (d) $U/t = 0$, (e) 5 and (f) 10 calculated by the method B (GCE-B): $q = 1.0$ (bold solid curves), 1.1 (dotted curves), 1.2 (dashed curves), 1.5 (chain curves) and 2.0 (solid curves).

Figure 4: The temperature dependences of the susceptibility $\chi_q$ of grand-canonical ensembles for (a) $U/t = 0$, (b) 5 and (c) 10 calculated by the method A (GCE-A), and those for (d) $U/t = 0$, (e) 5 and (f) 10 calculated by the method B (GCE-B): $q = 1.0$ (bold solid curves), 1.1 (dotted curves), 1.2 (dashed curves), 1.5 (chain curves) and 2.0 (solid curves).

Figure 5: The temperature dependence of $1/\chi_q$ in the atomic limit ($t/U = 0$) of grand-canonical ensembles for various $q$ values calculated by (a) the method A (GCE-A) and (b) the method B (GCE-B). The temperature dependence of $\Gamma_q(T)$ in the atomic limit ($t/U = 0$) for various $q$ values calculated by (c) the method A and (d) B. The $q$ dependence of the Curie constant $\Gamma_q(T)$ at $T/U = 0$ and 10 calculated by (e) the method A and (f) B. Chain curves in (e) and (f) express $\Gamma_q(\infty) = q^{4(q-1)}$ and $\Gamma_q(\infty) = q$, respectively (see text).

Figure 6: The temperature dependences of the specific heat $C_q$ of canonical ensembles for $h = 0$ with (a) $U/t = 0$, (b) 5 and (c) 10 calculated by the method A (CE-A), and those with (d) $U/t = 0$, (e) 5 and (f) 10 calculated by the method B (CE-B): $q = 1.0$ (bold solid curves), 1.1 (dotted curves), 1.2 (dashed curves), 1.5 (chain curves) and 2.0 (solid curves).

Figure 7: The temperature dependences of the susceptibility $\chi_q$ of canonical ensembles for (a) $U/t = 0$, (b) 5 and (c) 10 calculated by the method A (CE-A), and those for (d) $U/t = 0$, (e) 5 and (f) 10 calculated by the method B (CE-B): $q = 1.0$ (bold solid curves), 1.1 (dotted curves), 1.2 (dashed curves), 1.5 (chain curves) and 2.0 (solid curves).
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