Non-extensive thermodynamics of transition-metal nanoclusters

Hideo Hasegawa

Department of Physics, Tokyo Gakugei University
Koganei, Tokyo 184-8501, Japan

(March 23, 2022)

Abstract

In recent years, much study has been made by applying the non-extensive statistics (NES) to various non-extensive systems where the entropy and/or energy are not necessarily proportional to the number of their constituent subsystems. The non-extensivity may be realized in many systems such as physical, chemical and biological ones, and also in small-scale nanosystems.

After briefly reviewing the recent development in nanomagnetism and the NES, I have discussed, in this article, NES calculations of thermodynamical properties of a nanocluster containing noninteracting \( M \) dimers. With bearing in mind a transition-metal nanocluster, each of the dimers is assume to be described by the two-site Hubbard model (a Hubbard dimer). The temperature and magnetic-field dependences of the specific heat, magnetization and susceptibility have been calculated by changing \( M = 1, 2, 3 \) and \( \infty \), results for \( M = \infty \) corresponding to those of the conventional Boltzman-Gibbs statistics (BGS). It has been shown that the thermodynamical property of nanoclusters containing a small number of dimers is considerably different from that of macroscopic counterparts calculated within the BGS. The specific heat and susceptibility of spin dimers described by the Heisenberg model have been discussed also by employing the NES.

Contents

1. Introduction
   1.1 A brief review of nanomagnetism
   1.2 Non-extensive statistics

2. Non-extensive thermodynamics of Hubbard dimers
   2.1 Energy and entropy
   2.2 Specific heat
   2.3 Magnetization
   2.4 Susceptibility

3. Calculated results
   3.1 Temperature dependence

---

1To be submitted to Prog. Mat. Sci.: Festschrift Proceedings for David’s 60th
2E-mail: hasegawa@u-gakugei.ac.jp
1 Introduction

1.1 A brief review of nanomagnetism

In the last decade, there has been a considerable interest in atomic engineering, which makes it possible to create small-scale materials with the use of various methods (for reviews, see Refs. [1, 2, 3]). Small-scale magnetic systems ranging from grains (micros), nanosystems, molecular magnets and atomic clusters, display a variety of interesting properties. Magnetic nanosystems consist of small clusters of magnetic ions embedded within nonmagnetic ligands or on nonmagnetic substrates. Nanomagnetism shows interesting properties different from bulk magnetism. Nanoclusters consisting of transition metals such as Fe\textsubscript{N} (N=15-650) [4], Co\textsubscript{N} (N=20-200) [5], and Ni\textsubscript{N} (N=5-740) [6] 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 per atom are increased with reducing \( N \) [6]. It is shown that magnetic moments in Co monatomic chains constructed on Pt substrates are larger than those in monolayer Co and bulk Co [7]. Recently Au nanoparticles with average diameter of 1.9 \textit{nm} (including 212 atoms), which are protected by polyallyl amine hydrochloride (PAAHC), are reported to show ferromagnetism while bulk Au is diamagnetic [8]. This is similar to the case of gas-evaporated Pd fine particles with the average diameter of 11.5 \textit{nm} which show the ferromagnetism whereas bulk Pd is paramagnetic [9]. The magnetic property of four-Ni molecular magnets with the tetrahedral structure (abbreviated as Ni4) in 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 [10]. Their temperature-dependent susceptibility and magnetization process have been analyzed by using the Heisenberg model with the antiferromagnetic exchange couplings between Ni atoms [10]. Similar analysis has been made for magnetic molecules of FeN (\( N = 6, 8, 10 \) and 12) [11][12], and V6 [13]. Extensive studies have been made for single molecule magnets of Mn12 in \([\text{Mn}_{12}\text{O}_{12}\{(\text{CH}_3\text{COO})_{16}\text{H}_2\text{O}\}_4]\) [14] and Fe8 in \([\text{Fe}_8(tanc)_6\text{O}_2(\text{OH})_{12}]\text{Br}_9 \cdot 9\text{H}_2\text{O}\) [15]. Both Mn12 and Fe8 behave as large single spins with \( S = 10 \), and show quantum tunneling of magnetization and the square-root relaxation, which are current topics in nanomagnetism. Much attention has been recently paid
to single molecule magnets which are either dimers or behave effectively as dimers, due
to their potential use as magnetic storage and quantum computing. The iron \( S = \frac{5}{2} \)
dimer (Fe2) in \([\text{Fe}(\text{OMe})(\text{dbm})_2]_2\) [16] has a nonmagnetic, singlet ground state and its
thermodynamical property has been analyzed with the use of the Heisenberg model [17]-
[19]. Similar analysis has been made for transition-metal dimers of V2 [20], Cr2 [21], Co2
[22], Ni2 [24] and Cu2 [25].

1.2 Non-extensive statistics

As the size of systems becomes smaller, effects of fluctuations and contributions from
surface play more important roles. There are currently three approaches to discussing
nanothermodynamics for small-size systems: (1) a modification of the Boltzman-Gibbs
statistics (BGS) adding subdivision energy [26], (2) non-equilibrium thermodynamics in-
cluding work fluctuations [27], and (3) the non-extensive statistics (NES) generalizing
the BGS as to take account of the non-extensive feature of such systems [28]-[33]. A
comparison between these approaches have been made in Refs. [33][34].

Before discussing the NES, let’s recall the basic feature of the 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 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 Boltzman constant. The probability of finding the system with the energy \( E \) is given
by \( p(E) = \Omega(E_0 - E) / \Omega(E) \sim \exp(-E/k_BT) \) with \( E \ll E_0 \). When the physical quantity
\( Q \) of a system containing \( N \) particles is expressed by \( Q \propto N^\gamma \), they are classified into two
groups in the BGS: intensive (\( \gamma = 0 \)) and extensive ones (\( \gamma = 1 \)). The temperature and
energy are typical intensive and extensive quantities, respectively. This is not the case in
the NES, as will be shown below.

When a small-scale nanosystem is immersed in a reservoir, the temperature of the
nanosystem is expected to fluctuate around the temperature of the reservoir \( T_0 \) because
of the smallness of the nanosystem and its quasi-thermodynamical equilibrium states.
Then the BGS distribution mentioned above has to be averaged over the fluctuating
temperature. This idea has been expressed by [31][32][33]

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

with

\[
q = 1 + \frac{2}{N}, \quad (2)
\]

\[
f^B(\beta) = \frac{1}{\Gamma\left(\frac{N}{2}\right)} \left(\frac{N}{2\beta_0}\right)^{\frac{N}{2}} \beta^{\frac{N}{2} - 1} \exp\left(-\frac{N\beta}{2\beta_0}\right), \quad (3)
\]
\[
\beta_0 = \frac{1}{k_B T_0} = \int_0^\infty d\beta f(\beta) \beta \equiv E(\beta),
\]
(4)
\[
\frac{2}{N} = \frac{E(\beta^2) - E(\beta)^2}{E(\beta)^2},
\]
(5)
where \( \exp_q(x) \) denotes the \( q \)-exponential function defined by
\[
\exp_q(x) = [1 + (1 - q)x]^{\frac{1}{1-q}}, \quad \text{for } 1 + (1 - q)x > 0
\]
\[
= 0, \quad \text{otherwise}
\]
(6)
In Eqs. (1)-(6), \( q \) expresses the entropic index, \( f^B(\beta) \) the \( \Gamma \) (or \( \chi^2 \)) distribution function of the order \( N \), \( E(Q) \) the expectation value of \( Q \) averaged over \( f(\beta) \), \( \beta_0 \) the average of the fluctuating \( \beta \) and \( 2/N \) its variances. The \( \Gamma \) distribution of the order \( N \) is emerging from the sum of squares of \( N \) Gaussian random variables. In deriving Eqs. (1)-(5), we have assumed that \( N \) particles are confined within a small volume of \( L^3 \) \( (L < \xi) \) where the variable \( \beta \) uniformly fluctuates, \( \xi \) standing for the coherence length [32].

The important consequence of the NES is that energy and entropy are not proportional to \( N \) in nanosystems. The non-extensivity of the entropy was first demonstrated by Tsallis, who proposed the generalized entropy given by [28]
\[
S_q = k_B \left( \sum_i p_i^q - 1 \right) = -k_B \sum_i p_i^q \ln_q(p_i),
\]
(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 defined by Eq. (6). It is noted that in the limit of \( q = 1 \), Eq. (7) reduces to the entropy of BGS, \( S_{BG} \), given by
\[
S_1 = S_{BG} = -k_B \sum_i p_i \ln p_i.
\]
(8)
The non-extensivity in the Tsallis entropy is satisfied as follows. Suppose that the total system containing \( 2N \) particles is divided into two independent subsystems, each of which contains \( N \) particles, 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 \( S(2N) \) is given by [28]
\[
S(2N) = S(N) + S(N) + O \left( \frac{1}{N} \right),
\]
(9)
where \( S(N) \) stands for the entropy of the \( N \)-particle subsystem, the index \( q \) given by Eq. (2) being employed. Similarly the energy of the total system is expressed by
\[
E(2N) = E(N) + E(N) + O \left( \frac{1}{N} \right),
\]
(10)
The difference of \( E(2N) - 2E(N) \) is attributed to the surface contribution. This implies that the index \( \gamma \) in \( Q \propto N^\gamma \) is neither 0 nor 1 for \( Q = S \) and \( E \) in nanosystems within the NES.
The functional form of the probability distribution \( p(E) \) expressed by Eq. (1) was originally derived by the maximum-entropy method [28][29]. The probability of \( p_i [= p(\epsilon_i)] \) for the eigenvalue \( \epsilon_i \) in the NES is determined by imposing the variational condition to the entropy given by Eq. (7) with the two constraints [29]:

\[
\sum_i p_i = 1, \quad \frac{\sum_i p_i^q \epsilon_i}{\sum_i p_i^q} = E_q. \tag{11} \tag{12}
\]

The maximum-entropy method leads to the probability distribution \( p_i \) given by

\[
p_i \propto \exp_q \left[ -\beta_0 (\epsilon_i - E_q) \right], \tag{13}
\]

with

\[
\beta_0 = \frac{\beta}{c_q}, \quad c_q = \sum_i p_i^q, \tag{14} \tag{15}
\]

where \( \beta \) denotes the Lagrange multiplier relevant to the constraint given by Eq. (12). It has been shown that the physical temperature \( T \) of the nanosystem is given by [35]

\[
T = \frac{c_q}{k_B \beta}, \quad \text{(AMP)} \tag{16}
\]

In the limit of \( q = 1 \), we get \( \exp_q [x] = e^x \), \( c_q = 1 \) and \( p_i \) given by Eqs. (13)-(16) reduces to the results obtained in the BGS, related discussions being given in Sec. 4.

In previous papers [36, 37, 38], I have applied the NES to the Hubbard model, which is one of the most important models in solid-state physics (for a recent review, see Ref. [39]). The Hubbard model consists of the tight-binding term expressing electron hoppings and the short-range interaction between two electrons with opposite spins. The Hubbard model provides us with good qualitative description for many interesting phenomena such as magnetism, electron correlation, and superconductivity. In particular, the Hubbard model has been widely employed for a study on transition-metal magnetism. In the limit of strong interaction \( (U/t \ll 1) \), the Hubbard model with the half-filled electron occupancy reduces to the Heisenberg or Ising model. The two-site Hubbard model has been adopted for a study on some charge-transfer salts like tetracyanoquinodimethan (TCNQ) with dimerized structures [40]-[42]. Their susceptibility and specific heat were analyzed by taking into account the interdimer hopping within the BGS. The NES calculations have been made for thermodynamical properties of canonical [36][38] and grand-canonical ensembles [37] of Hubbard dimers, each of which is described by the two-site Hubbard model. It has been shown that the temperature dependences of the specific heat and susceptibility is significantly different from those calculated by the BGS when the entropic index \( q \) departs from unity for small \( N \) [Eq. (2)], the NES in the limit of \( q = 1 \) reducing to the BGS.
The purpose of the present paper is to show (1) how thermodynamical property of a nanocluster containing a small number of Hubbard dimers is different from that of macroscopic systems, and (2) how thermodynamical property of a given nanocluster is changed when \( M \), the number of Hubbard dimers contained in it, is varied. The paper is organized as follows. In Sec. 2, I apply the NES to nanoclusters, providing expressions for the energy, entropy, magnetization, specific heat and susceptibility. Numerical calculations of the temperature and magnetic-field dependences of thermodynamical quantities are reported for various \( M \) values. The final Sec. 4 is devoted to discussions and conclusions. In the Appendix, the NES has been applied to a cluster containing spin dimers described by the Heisenberg model.

2 Nonextensive thermodynamics of Hubbard dimers

2.1 Energy and entropy

I have adopted a system consisting of sparsely distributed \( N_c \) nanoclusters, each of which contains independent \( M \) dimers. It has been assumed that the distance between nanoclusters is larger than \( \xi \), the coherence length of the fluctuating \( \beta \) field, and that the linear size of the clusters is smaller than \( \xi \). Physical quantities such as the entropy and energy are extensive for \( N_c \), but not for \( M \) in general [32].

The Hamiltonian of the cluster is given by

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

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

where \( H^{(d)}_{\ell} \) denotes the two-site Hamiltonian for the \( \ell \)th dimer, \( n_{j\sigma} = a_{j\sigma} \dagger a_{j\sigma} \), \( a_{j\sigma} \) the annihilation operator of an electron with spin \( \sigma \) on a site \( j \) \((\epsilon \in \ell)\), \( t \) the hopping integral, \( U \) the intraatomic interaction, \( \mu_B \) the Bohr magneton, and \( B \) an applied magnetic field. In the case of the half-filled occupancy, in which the number of electrons is \( N_e = 2 \), six eigenvalues of \( H^{(d)}_{\ell} \) are given by

\[
\epsilon_{i\ell} = 0, 2\mu_B B, -2\mu_B B, U, \frac{U}{2} + \Delta, \frac{U}{2} - \Delta, \quad \text{for } i = 1 - 6, \ell = 1 - M
\]

where \( \Delta = \sqrt{U^2/4 + 4t^2} \) [40][42]. The number of eigenvalues of the total Hamiltonian \( H \) is \( 6^M \).

First we employ the BGS, in which the canonical partition function for \( H \) is given by [40][42]

\[
Z_{BG} = \text{Tr} \exp(-\beta H),
\]
\[
\sum_{i_1=1}^{6} \cdots \sum_{i_M=1}^{6} \exp[-\beta(\epsilon_{i_1} + \cdots + \epsilon_{i_M})], \quad (21)
\]

\[
Z_{BG}^{(d)} = [Z_{BG}^{(d)}]_1^M, \quad (22)
\]

\[
Z_{BG}^{(d)} = 1 + 2 \cosh(2\beta \mu_B B) + e^{-\beta U} + 2 e^{-\beta U/2} \cosh(\beta \Delta), \quad (23)
\]

where \( \beta = 1/k_B T \), \( \text{Tr} \) denotes the trace and \( Z_{BG}^{(d)} \) the partition function for a single dimer. By using the standard method in the BGS, we can obtain various thermodynamical quantities of the system [40, 41, 42]. Because of a power expression given by Eq. (22), the energy and entropy are proportional to \( M \): \( E_{BG} = M E_{BG}^{(d)} \) and \( S_{BG} = M S_{BG}^{(d)} \) where \( E_{BG}^{(d)} \) and \( S_{BG}^{(d)} \) are for a single dimer. This is not the case in the NES as will be discussed below.

Next we adopt the NES, where the entropy \( S_q \) for the quantum system is defined by [28][29]

\[
S_q = k_B \left( \frac{\text{Tr} (\rho^q) - 1}{1 - q} \right). \quad (24)
\]

Here \( \rho_q \) stands for the generalized canonical density matrix, whose explicit form will be determined shortly [Eq. (27)]. We will impose the two constraints given by

\[
\begin{align*}
\text{Tr} (\rho_q) &= 1, \quad (25) \\
\frac{\text{Tr} (\rho^q H)}{\text{Tr} (\rho^q)} &= < H >_q - E_q, \quad (26)
\end{align*}
\]

where the normalized formalism is adopted [29]. The variational condition for the entropy with the two constraints given by Eqs. (25) and (26) yields

\[
\rho_q = \frac{1}{X_q} \exp_q \left[ - \left( \frac{\beta}{c_q} \right) (H - E_q) \right], \quad (27)
\]

with

\[
\begin{align*}
X_q &= \text{Tr} \left( \exp_q \left[ - \left( \frac{\beta}{c_q} \right) (H - E_q) \right] \right), \quad (28) \\
c_q &= \text{Tr} (\rho^q) = X_q^{1-q}, \quad (29)
\end{align*}
\]

where \( \exp_q(x) \) is the \( q \)-exponential function given by Eq. (6) and \( \beta \) is a Lagrange multiplier given by

\[
\beta = \frac{\partial S_q}{\partial E_q}. \quad (30)
\]

The trace in Eq. (28) and (29) is performed over the \( 6^M \) eigenvalues, for example, as

\[
\begin{align*}
X_q &= \sum_{i_1=1}^{6} \cdots \sum_{i_M=1}^{6} \exp_q \left[ - \left( \frac{\beta}{c_q} \right) (\epsilon_{i_1} + \cdots + \epsilon_{i_M} - E_q) \right], \quad (31) \\
&= \sum_{i} \exp_q \left[ - \left( \frac{\beta}{c_q} \right) (\epsilon_i - E_q) \right], \quad (32)
\end{align*}
\]

7
where the following conventions are adopted:

\[ \epsilon_i = \epsilon_{i_1} + \cdots + \epsilon_{i_M}, \]
\[ \sum_i = \sum_{i_1=1}^6 \cdots \sum_{i_M=1}^6. \]

It is noted that in the limit of \( q = 1 \), Eq. (31) reduces to

\[ X_1 = Z_{BG} \exp[\beta \epsilon_1] = [Z_{BG}^{(d)} \exp (\beta E_{BG}^{(d)})]^M. \]

For \( q \neq 1 \), however, \( X_q \) cannot be expressed as a power form because of the property of the \( q \)-exponential function:

\[ \exp_q(x + y) \neq \exp_q(x) \exp_q(y). \quad \text{(for } q \neq 1) \]

It is necessary to point out that \( E_q \) in Eq. (26) includes \( X_q \) which is expressed by \( E_q \) in Eq. (28). Then \( E_q \) and \( X_q \) have to be determined self-consistently by Eqs. (26)-(29) with the \( T - \beta \) relation given by Eq. (16) for a given temperature \( T \). The calculation of thermodynamical quantities in the NES generally becomes more difficult than that in BGS.

### 2.2 Specific heat

The specific heat in the NES is given by [36]

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

Because \( E_q \) and \( X_q \) are determined by Eqs. (26)-(29), we get simultaneous equations for \( dE_q/d\beta \) and \( dX_q/d\beta \), given by

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

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

with

\[ a_{11} = q\beta X_q^{q-2} \sum_i w_i^{2q-1} \epsilon_i, \]

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

\[ a_{21} = \beta X_q^q, \]

\[ a_{22} = 0, \]

\[ b_1 = -qX_q^{q-2} \sum_i w_i^{2q-1} \epsilon_i(\epsilon_i - E_q), \]

\[ w_i = \exp_q \left[ -\left( \frac{\beta}{c_q} \right) (\epsilon_i - E_q) \right], \]

\[ X_q = \sum_i w_i. \]
The specific heat is then given by

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

(47)

with

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

(48)

In the limit of \( q \to 1 \), Eqs. (38)-(46) yield the specific heat in the BGS, given by [37]

\[ C_{BG} = \frac{dE_{BG}}{dT} = k_B\beta^2(< \epsilon_i^2 >_1 - < \epsilon_i >^2_1), \]  

(49)

where \(< \cdot >_1\) is defined by Eq. (26) with \( q = 1 \):

\[ < Q_i >_1 = X_1^{-1} \sum_i \exp[-\beta(\epsilon_i - E_1)] Q_i = Z_{BG}^{-1} \sum_i \exp(-\beta\epsilon_i) Q_i. \]  

(50)

### 2.3 Magnetization

The field-dependent magnetization \( m_q \) in the NES is given by [36]

\[ m_q = -\frac{\partial E_q}{\partial B} + (k_B \beta)^{-1} \frac{\partial S_q}{\partial B}, \]  

(51)

\[ = -\frac{\partial E_q}{\partial B} + \beta^{-1}X_q^{-q} \frac{\partial X_q}{\partial B}. \]  

(52)

By using Eqs. (26)-(29), we get the simultaneous equations for \( \partial E_q/\partial B \) and \( \partial X_q/\partial B \) given by

\[ \frac{\partial E_q}{\partial B} = a_{11} \frac{\partial E_q}{\partial B} + a_{12} \frac{\partial X_q}{\partial B} + d_1, \]  

(53)

\[ \frac{\partial X_q}{\partial B} = a_{21} \frac{\partial E_q}{\partial B} + a_{22} \frac{\partial X_q}{\partial B} + d_2, \]  

(54)

with

\[ d_1 = -X_q^{-1} \sum_i w_i^q \mu_i + \beta q X_q^{-2} \sum_i w_i^{2q-1} \epsilon_i \mu_i, \]  

(55)

\[ d_2 = \beta X_q^{q-1} \sum_i w_i^q \mu_i, \]  

(56)

where \( \mu_i = -\partial \epsilon_i / \partial B \), and \( a_{ij} \ (i, j = 1, 2) \) are given by Eqs. (40)-(43). From Eqs. (51)-(56), we obtain \( m_q \) given by

\[ m_q = \left( -c_{12} + \beta^{-1}X_q^{-q}(1-c_{11}) \right) \frac{1}{1 - c_{11} - c_{12}c_{21}} d_2, \]  

(57)

\[ = X_q^{-1} \sum_i w_i^q \mu_i = < \mu_i >_q . \]  

(58)
In the limit of \( q \to 1 \), Eqs. (55) and (56) reduce to

\[
\begin{align*}
d_1 &= -\langle \mu_i \rangle_1 + \beta \langle \epsilon_i \mu_i \rangle_1, \\
d_2 &= \beta X_1 \langle \mu_i \rangle_1,
\end{align*}
\]

where \( \langle \cdot \rangle_1 \) is given by Eq. (50). By using Eq. (58), we get

\[
\begin{align*}
m_{BG} &= \langle \mu_i \rangle_1, \\
&= \frac{4 \mu_B \sinh(2 \beta B)}{Z_{BG}},
\end{align*}
\]

where \( Z_{BG} \) and \( \langle \cdot \rangle_1 \) are given by Eqs. (20) and (50), respectively.

### 2.4 Susceptibility

The high-field susceptibility in the NES is given by

\[
\chi_q(B) = \frac{\partial m_q}{\partial B}.
\]

The zero-field susceptibility \( \chi_q(B = 0) \) is given by [36]

\[
\chi_q = \chi_q(B = 0) = -E_q^{(2)} + \beta^{-1}X_q^{-q}X_q^{(2)},
\]

where \( E_q^{(2)} = \partial^2 E_q/\partial B^2 \mid_{B=0} \) and \( X_q^{(2)} = \partial^2 X_q/\partial B^2 \mid_{B=0} \). With the use of Eqs. (26)-(29), we get simultaneous equations for \( E_q^{(2)} \) and \( X_q^{(2)} \) given by

\[
\begin{align*}
E_q^{(2)} &= a_{11}E_q^{(2)} + a_{12}X_q^{(2)} + f_1, \\
X_q^{(2)} &= a_{21}E_q^{(2)} + a_{22}X_q^{(2)} + f_2,
\end{align*}
\]

with

\[
\begin{align*}
f_1 &= -2 \beta q X_q^{q-2} \sum_i w_i^{2q-1} \mu_i^2, \\
f_2 &= \beta^2 q X_q^{2(q-1)} \sum_i w_i^{2q-1} \mu_i^2,
\end{align*}
\]

where \( a_{ij} \) \((i, j = 1, 2)\) are given by Eqs. (40)-(43). From Eqs. (64)-(68), we get

\[
\chi_q = \frac{f_2}{a_{21}} = \beta q X_q^{q-2} \sum_i w_i^{2q-1} \mu_i^2 \mid_{B=0}.
\]

In the limit of \( q = 1 \), Eq. (69) yields the susceptibility in BGS:

\[
\begin{align*}
\chi_{BG} &= \beta < \mu_i^2 \mid_{B=0} >_1, \\
&= \left( \frac{\mu_B^2}{k_B T} \right) \frac{8}{3 + e^{-\beta U} + 2e^{-\beta U/2} \cosh(\beta \Delta)}.
\end{align*}
\]
3 Calculated results

3.1 Temperature dependence

In order to study how thermodynamical quantities of a cluster containing $M$ Hubbard dimers depend on $M$, I have made some NES calculations, assuming the $M-q$ relation given by

$$q = 1 + \frac{1}{M},$$

(72)

which is derived from Eq. (2) with $M = 2N$ for dimers. Simultaneous equations for $E_q$ and $X_q$ given by Eqs. (26)-(29) have been solved by using the Newton-Raphson method with initial values of $E_1$ and $X_1$ obtained from BGS ($q = 1$) corresponding to $M = \infty$ in Eq. (72). Calculated quantities are given per dimer.

Figures 1(a), 1(b) and 1(c) show the temperature dependence of the specific heat $C_q$ for $U/t = 0$, 5 and 10, respectively, with various $M$ values. The specific heat for $M = \infty$ shown by bold solid curves, expresses the result in BGS, and it has a peak at lower temperatures for the larger interaction, as previous BGS calculations showed [41]. Note that the horizontal scales of Fig. 1(c) are enlarged compared to those of Figs. 1(a) and 1(b). The peak becomes broader for smaller $M$.

The temperature dependence of the susceptibility $\chi_q$ for $U/t = 0$, 5 and 10 is plotted in Figs. 2(a), 2(b) and 2(c), respectively. The susceptibility for $M = \infty$ (BGS) shown by the bold solid curve, has a larger peak at lower temperatures for larger $U$ [41]. Note that the horizontal and vertical scales of Fig. 2(c) are different from those of Figs. 2(a) and 2(b). We note that for smaller $M$, the peak in $\chi_q$ becomes broader, which is similar to the behavior of the specific heat shown in Figs. 1(a)-1(c).

When the $M$ value is varied, maximum values of the specific heat ($C^*_q$) and the susceptibility ($\chi^*_q$) are changed, and the temperatures ($T^*_C$ and $T^*_\chi$) where these maxima are realized, are also changed. Figure 3(a) depicts $T^*_C$ and $T^*_\chi$ for $U/t = 5$ as a function of $1/M$. It is shown that with increasing $1/M$, $T^*_\chi$ is much increased than $T^*_C$. Similarly, the $1/M$ dependences of $C^*_q$ and $\chi^*_q$ for $U/t = 5$ are plotted in Fig. 3(b), which shows that maximum values of $C_q$ and $\chi_q$ are decreased with decreasing $M$. This trend against $1/M$ is due to the fact that a decrease in $M (= 2N)$ yields an increase in fluctuations of $\beta$ fields, and then peaked structures of the specific heat and susceptibility realized in the BGS, are smeared out by $\beta$ in Eq. (1).

3.2 Magnetic-field dependence

Next I discuss the magnetic-field dependence of physical quantities. Figure 4 shows the $B$ dependence of the magnetization $m_q$ for $U/t = 0$, 5 and 10 with $M = 2$ at $k_B T/t = 1$. For $U/t = 0$, $m_q$ in the NES is smaller than that in the BGS at $\mu_B B/t < 1$, but at $\mu_B B/t > 1$ the former becomes larger than the latter. In contrast, in cases of $U/t = 5$ and 10, $m_q$ in the NES is larger than that in the BGS for $\mu_B B/t > 0$. In order to study the $B$ dependence in more details, I show in Fig. 5 the $B$ dependence of the six eigenvalues of
\[ \epsilon_i \text{ for } U/t = 5 \text{ [Eq. (19)]}. \] We note the crossing of the lowest eigenvalues of \( \epsilon_3 \) and \( \epsilon_6 \) at the critical field:

\[ \mu_B B_c = \sqrt{\frac{U^2}{16} + t^2} - \frac{U}{4}, \] (73)

leading to \( \mu_B B_c / t = 0.351 \) for \( U/t = 5.0 \). At \( B < B_c \) (\( B > B_c \)), \( \epsilon_6 \) (\( \epsilon_3 \)) is the ground state. At \( B = B_c \) the magnetization \( m_q \) is rapidly increased as shown in Figs. 6(a) and 6(b) for \( k_B T/t = 1.0 \) and 0.1, respectively: the transition at lower temperatures is more evident than at higher temperatures. This level crossing also yields a peak in \( \chi_q \) [Figs. 6(c) and 6(d)] and a dip in \( C_q \) [Figs. 6(e) and 6(f)]. It is interesting that the peak of \( \chi_q \) for \( M = 2 \) is more significant than that for \( M = \infty \) whereas the dip of \( C_q \) for \( M = 2 \) is broader than that for \( M = \infty \). When the temperature becomes higher, these peak structures become less evident as expected. Similar phenomenon in the field-dependent specific heat and susceptibility have been pointed out in the Heisenberg model within the BGS [43].

In the case of the quarter-filled occupancy (\( N_e = 1 \)), the eigenvalues are

\[ \epsilon_i = -t - \mu_B B, \]

\[ -t + \mu_B B, \]

\[ t - \mu_B B, \]

\[ t + \mu_B B \]

for \( i = 1 - 4 \). Although the level crossing occurs between \( \epsilon_2 \) and \( \epsilon_3 \) at \( \mu_B B = t \), it does not show any interesting behavior because the crossing occurs between the excited states. The case for the three-quarter-filled occupancy (\( N_e = 3 \)) is the same as that of the quarter-filled occupancy because of the electron-hole symmetry of the model.

Figure 6(b) reminds us the quantum tunneling of magnetization observed in magnetic molecular clusters such as Mn12 and Fe8 [14], which originates from the level crossings of magnetic molecules when a magnetic field is applied [14].

4 Discussions and conclusions

I have applied the NES to Hubbard dimers for a study of their thermodynamical properties. The current NES is, however, still in its infancy, having following unsettled issues.

(i) For relating the physical temperature \( T \) to the Lagrange multiplier \( \beta \), I have employed the \( T - \beta \) relation given by Eq. (16). There is an alternative proposal with the \( T - \beta \) relation given by [29]

\[ T = \frac{1}{k_B \beta}, \] (TMP) (74)

which is the same as in the BGS. At the moment, it has not been established which of the AMP and TMP methods given by Eqs. (16) and (74), respectively, is appropriate as the \( T - \beta \) relation in the current NES. It has been demonstrated that the negative specific heat of a classical gas model realized in the TMP method [44], is remedied in the AMP method [35]. Recent theoretical analyses also suggest that the AMP method is better than the TMP method [45][46]. The TMP method yields an anomalously large Curie constant of the susceptibility in the free spin model [37][47] and in the Hubbard model [36, 37]. In my previous papers [36]-[38], NES calculations have been made by using the TMP and
AMP methods. It has been shown that both methods yield qualitatively similar results although there are some quantitative difference between the two: the non-extensivity in the TMP method generally appears more significant than that in the AMP method.

(ii) The $N-q$ relation given by Eq. (2) was obtained in Eqs. (1)-(5) with the $\Gamma$ distribution $f^B(\beta)$ given by Eq. (3). Alternatively, by using the large-deviation approximation, Touchette [48] has obtained the distribution function $f^T(\beta)$, in place of $f^B(\beta)$, given by

$$f^T(\beta) = \frac{\beta_0}{\Gamma\left(\frac{N}{2}\right)} \left(\frac{N\beta_0}{2}\right)^{N/2} \beta^{-N/2-2} \exp\left(-\frac{N\beta_0}{2\beta}\right). \quad (75)$$

For $N \to \infty$, both $f^B(\beta)$ and $f^T(\beta)$ distribution functions 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 (see Fig. 4 of Ref.[38]). 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 $\epsilon$, the $\Gamma$ distribution $f^B$ in Eq. (1) yields the power form of $w(\epsilon) \sim \epsilon^{-1/\epsilon^2}$ while $f^T$ substituted to Eq. (1) leads to the stretched exponential form of $w(\epsilon) \sim e^{\epsilon \sqrt{\epsilon}}$. This issue of $f$ versus $f^T$ is related to the superstatistics, which is currently studied with much interest [49].

To summarize, I have discussed thermodynamical properties of a nanocluster containing $M$ dimers, applying the NES to the Hubbard model. It has been demonstrated that the thermodynamical properties of a nanocluster with a small $M$ calculated by the NES may be considerably different from those obtained by the BGS. It is interesting to compare our theoretical prediction with experimental results for samples containing a small number of transition-metal dimers. Unfortunately samples with such a small number of dimers have not been reported: samples having been so far synthesized include macroscopic numbers of dimers, to which the present analysis cannot be applied. I expect that it is possible to form a dimer assembly by STM manipulation of individual atoms [50]. Scanning probes may be used also as dipping pens to write small dimerized structures [51]. Theoretical and experimental studies on nanoclusters with changing $M$ could clarify a link between the behavior of the low-dimensional infinite systems and finite-size nanoscale systems. I hope that the unsettle issues (i) and (ii) in the current NES mentioned above are expected to be resolved by future experiments on nanosystems with changing their sizes. It would be interesting to adopt quantum-master-equation and quantum-Langevin-equation approaches, and/or to perform large-scale molecular-dynamical simulations, for nanoclusters described by the Hubbard model.

Acknowledgements

It is my great pleasure that on the occasion of the 60th birthday of Professor David G. Pettifor, I could dedicate the present paper to him, with whom I had an opportunity of collaborating in Imperial College London for one year from 1980 to 1981.
Appendix: NES for Heisenberg dimers

I have considered a cluster containing $M$ spin dimers (called Heisenberg dimers) described by the Heisenberg model ($s = 1/2$) given by

$$H = \sum_{\ell=1}^{M} H^{(d)}_{\ell},$$

$$H^{(d)}_{\ell} = -J s_1 \cdot s_2 - g\mu_B B (s_{1z} + s_{2z}), \quad (1, 2 \in \ell)$$

where $J$ stands for the exchange interaction, $g$ (=2) the g-factor, $\mu_B$ the Bohr magneton, and $B$ an applied magnetic field. Four eigenvalues of $H^{(d)}_{\ell}$ are given by

$$\epsilon_{i\ell} = -\frac{J}{4} - g\mu_B B m_i, \quad \text{with} \quad m_1 = 1, 0, -1 \text{ for } i = 1, 2, 3,$$

$$= -\frac{3J}{4} - g\mu_B B m_i. \quad \text{with} \quad m_4 = 0 \text{ for } i = 4,$$

In the BGS the canonical partition function is given by [17]-[19]

$$Z_{BG} = [Z_{BG}^{(d)}]^M,$$

$$Z_{BG}^{(d)} = \exp \left( \frac{\beta J}{4} \right) \left[ 1 + 2 \cosh(g\mu_B B) \right] + \exp \left( -\frac{3\beta J}{4} \right),$$

with which thermodynamical quantities are easily calculated. The susceptibility is, for example, given by

$$\chi_{BG} = M \chi_{BG}^{(d)},$$

$$\chi_{BG}^{(d)} = \frac{\mu_B^2}{k_B T} \left( \frac{8}{3 + \exp(-J/k_B T)} \right).$$

The calculation of thermodynamical quantities in the NES for the Heisenberg model goes parallel to that discussed in Sec. 2 if we employ eigenvalues given by Eq. (78). For example, by using Eq. (69), we get the susceptibility for the Heisenberg model, given by

$$\chi_q = g^2 \mu_B^2 \left( \frac{q\beta}{c_q} \right) \left( \frac{2}{X_q} \right) \left( \frac{1}{X_q} \sum_i u_i^{2q-1} m_i^2 \right).$$

In the case of $M = 1$ (a single dimer), we get

$$\chi_q^{(d)} = g^2 \mu_B^2 \left( \frac{q\beta}{c_q} \right) \left( \frac{2}{X_q} \right) \left( \exp_q \left[ \frac{\beta}{c_q} \left( \frac{J}{4} + E_q \right) \right] \right)^{2q-1},$$

with

$$X_q = 3 \exp_q \left[ \frac{\beta}{c_q} \left( \frac{J}{4} + E_q \right) \right] + \exp_q \left[ \frac{\beta}{c_q} \left( \frac{3J}{4} - E_q \right) \right],$$

$$E_q = \frac{1}{X_q} \{ \left( -\frac{3J}{4} \right) \left( \exp_q \left[ \frac{\beta}{c_q} \left( \frac{J}{4} + E_q \right) \right] \right)^q \},$$

$$+ \left( \frac{3J}{4} \right) \left( \exp_q \left[ \frac{\beta}{c_q} \left( \frac{3J}{4} - E_q \right) \right] \right)^q \}.$$
In the limit of $q = 1$, Eq. (84) reduces to $\chi_{BG}^{(d)}$ given by Eq. (82).

The Curie constant $\Gamma_q$ defined by $\chi_q = (\mu_B^2/k_B)(\Gamma_q/T)$ for $T \gg J$ is given by

$$\Gamma_q = 2Mq,$$  \hspace{1cm} (AMP) \hspace{1cm} (87)

$$= 2Mq4^{M(q-1)}.$$ \hspace{1cm} (TMP) \hspace{1cm} (88)

Equations (87) and (88) are derived with the use of the $T − \beta$ relation given by Eqs. (16) and (74), respectively. These are consistent with results obtained for Hubbard dimers [37].

Figures 7(a) and 7(b) show the temperature dependence of the specific heat $C_q$ and susceptibility $\chi_q$ of Heisenberg dimers calculated with the use of Eq. (83) for $M = 1, 2, 3$ and $\infty$ ($M = \infty$ corresponding to the BGS with $q = 1.0$). We note that the results of Heisenberg dimers are quite similar to those of the Hubbard dimer for $U/t = 5$ and 10 shown in Figs. 2(b), 2(c), 2(e) and 2(f). This is not surprising because the Hubbard model with the half-filled electron occupancy in the strong-coupling limit reduces to the Heisenberg model.

References

[1] Bader SD. Surf. Sci. 2002;500:172.

[2] Kachkachi H, Garanin DA. e-print: cond/mat/0310694.

[3] Luban M. J. Magn. Magn. Mat. 2004;272-276:e635.

[4] de Heer WA, Milani P, Châtelain A. Phys. Rev. Lett. 1990;65:488.

[5] Bucher JP, Douglass DC, Bloomfield LA. Phys. Rev. Lett. 1991;66:3052.

[6] Aspel SE, Emmert JW, Deng J, Bloomfield LA. Phys. Rev. Lett. 1996;76:1441.

[7] Gambardella P, Dallmeyer A, Malti M, Malagoll MC, Eberhardt W, Kern K, Carbone C. Nature 2002;416:301.

[8] Yamamoto Y, Miura T, Suzuki H, Kawamura N, Nakamura T, Kobayashi K, Teranishi T, Hori H. Phys. Rev. Lett. 2002;93:116801.

[9] Shinohara T, Sato T, Phys. Rev. Lett. 2003;91:197201.

[10] Postnikov AV, Brüger M, Schnack J., e-print: cond-mat/0404343.

[11] Lascialfari A, Gatteschi D, Borsa F, Cornia A, Phys. Rev. B 199755, 14341 ().

[12] Gatteschi D, Sessoli R, Cornia A. Chem. Commun. 2000;9:725.

[13] Luban M, Borsa F, Bud’ko S, Canfield P, Jun S, Jung JK, Kügerler P, Mentrup D, Müller A, Modler R, Procissi D, Suh BJ, Torikachvili M. Phys. Rev. B 2002;66:054407.
[14] Wernsdorfer W, Aliaga-Alcalde A, Hendrickson DN, Christou G. Nature 2002;416:406; related references therein.

[15] Caciuffo R, Amoretti G, Murani A. Phys. Rev. Lett. 1998;81:4744.

[16] Gall FL, DeBiani FF, Caneschi A, Cinelli P, Cornia A, Fabretti AC, Gatteschi D. Inorg. Chim. Acta 1997;262:123; Lascialfari A, Tabak F, Abbati GL, Borsa F, Corti M, Gatteschi D. J. Appl. Phys. 1999;85:4539.

[17] Mentrup D Schnack, J, Luban M. Physica A 1999;272:153.

[18] Efremov DV, Klemm RA. Phys. Rev. B 2002;66:174427; cond-mat/0409168.

[19] Dai D, Whangbo M. J. Chem. Phys. 2003;118:29.

[20] Furukawa Y, Iwai A, Kumagai K, Yabubovsky A. J. Phys. Soc. Jpn. 1996;65:2393; Tennant DA, Nagler SE, Garrett AW, Barnes T, Torardi CC. Phys. Rev. Lett. 1997;78:4998; Garrett AW, Nagler SE, Tennant DA, Sales BC, Barnes T. Phys. Rev. Lett. 1997;79:745.

[21] Bailey MS, Obrovac MN, Baillet E, Reynolds TK, DiSalvo FJ. Inorg. Chem. 2003;42:5572; Glerup J, Goodson PA, Hodgson DJ, Masood MA, Michelsen K. Inorganica 2005;358:295.

[22] Beckmann U, Brooker S. Coordination Chemistry 2003;245:17.

[23] Lazarov ND, Spasojevic V, Kusigerski V, Matić VM, Milić M. J. Magn. Magn. Matt. 2004;272-276:1065.

[24] Dey SK, Fallah MSE, Ribas J, Matsushita T, Gramlich V, Mitra S. Inorganica Chimica 2004;357:1517.

[25] Zheludev A, Shirane G, Sasago Y, Hase M, Uchinokura K. Phys. Rev. B 1996;53:11642.

[26] Hill TL. Nano Lett. 2001;1:273; ibid. 2002;2:609.

[27] Jarzynski C. Phys. Rev. Lett. 1997;78:2690; Phys. Rev. E 1997;56:5018.

[28] Tsallis C. J. Stat. Phys. 1988;52:479.

[29] Tsallis C, Mendes RS, Plastino AR. Physica A 1998;261:534.

[30] For a recent review on the NES, see Tsallis C. Physica D 2004;193:3.
[31] Wilk G, Wlodarczyk Z. Phys. Rev. Lett. 2000;84:2770.

[32] Beck C. Europhys. Lett. 2002;57:329.

[33] Rajagopal AK, Pande CS, Abe S. eprint cond-mat/0403738.

[34] Ritort F. e-print cond-mat/0401311.

[35] Abe S, Martínez S, Pennini F, Plastino A. Phys. Lett. A 2001;281:126.

[36] Hasegawa H. cond-mat/0408699.

[37] Hasegawa H. Physica A 2005;351:273.

[38] Hasegawa H. Prog. Theor. Phys. suppl. 2005;XXX:YYY (in press).

[39] Kakehashi Y. Adv. Phys. 2004;53:497; related references therein.

[40] Suzuki Y. Phys. Lett. 1972;38A:293.

[41] Shiba H, Pincus PA. Phys. Rev. B 1972;5:1966.

[42] Bernstein U, Pincus P. Phys. Rev. B 1974;10:3626.

[43] Kuzmenko and NK, Mikhajlov VM. e-print cond-mat/0401468.

[44] Abe S. Phys. Lett. A 1999;263:424; ibid. 2000;267:456(erratum).

[45] H. Suyari, cond-mat/0502298.

[46] T. Wada and A. M. Scarfone, cond-mat/0502394.

[47] Martinez S, Pennini F, Plastino A. Physica A 2000;282:193.

[48] Touchette H. e-print cond-mat/0212301.

[49] Beck C, Cohen EGD. e-print cond-mat/0205097; Touchette H, Beck C. e-print cond-mat/0408091.

[50] Manoharan HC, Lutz CP, Eiger DM. Nature 2000;403:512.

[51] Piner RD, Zhu J, Xu F, Hong S, Mirkin CA. Science 1999;283:661.
Figure 1: The temperature dependence of the specific heat \( C_q \) per dimer for (a) \( U/t = 0 \), (b) 5 and (c) 10, calculated for \( M = 1 \) (solid curves), \( M = 2 \) (chain curves), \( M = 3 \) (dashed curves) and \( M = \infty \) (bold solid curves), results for \( M = \infty \) denoting those in the BGS.

Figure 2: The temperature dependence of the susceptibility \( \chi_q \) per dimer for (a) \( U/t = 0 \), (b) 5 and (c) 10, calculated for \( M = 1 \) (solid curves), \( M = 2 \) (chain curves), \( M = 3 \) (dashed curves) and \( M = \infty \) (bold solid curves), results for \( M = \infty \) denoting those in the BGS.

Figure 3: (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) \( (U/t = 5) \)

Figure 4: The magnetic-filed dependence of the magnetization \( m_q \) for (a) \( U/t = 0 \), (b) 5, and (c) 10 with \( k_B T/t = 1 \) for \( M = 2 \) (solid curves) and \( \infty \) (dashed curves).

Figure 5: The magnetic-filed dependence of the eigenvalues \( \epsilon_i \) \( (i = 1 - 6) \) for \( U/t = 5 \), \( B_c \) denoting the critical field where a level crossing between \( \epsilon_3 \) and \( \epsilon_6 \) occurs.

Figure 6: The magnetic-filed 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 \( \chi_q \) for \( k_B T/t = 1.0 \) and (d) \( k_B T/t = 0.1 \), and (e) the specific heat \( C_q \) for \( k_B T/t = 1.0 \) and (f) \( k_B T/t = 0.1 \) with \( U/t = 5 \), calculated for \( M = 2 \) (solid curves) and \( \infty \) (dashed curves).

Figure 7: The temperature dependence of (a) the specific heat and (b) susceptibility of Heisenberg dimers for various \( M \): \( M = 1 \) (bold solid curves), \( M = 2 \) (chain curves), \( M = 3 \) (dashed curves), and \( M = \infty \) (solid curves).
This figure "fig1.gif" is available in "gif" format from:

http://arxiv.org/ps/cond-mat/0506553v3
This figure "fig2.gif" is available in "gif" format from:

http://arxiv.org/ps/cond-mat/0506553v3
This figure "fig3.gif" is available in "gif" format from:

http://arxiv.org/ps/cond-mat/0506553v3
This figure "fig4.gif" is available in "gif" format from:

http://arxiv.org/ps/cond-mat/0506553v3
This figure "fig5.gif" is available in "gif" format from:

http://arxiv.org/ps/cond-mat/0506553v3
This figure "fig6.gif" is available in "gif" format from:

http://arxiv.org/ps/cond-mat/0506553v3
This figure "fig7.gif" is available in "gif" format from:

http://arxiv.org/ps/cond-mat/0506553v3