Polaronic Heat Capacity in The Anderson - Hasegawa Model

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Abstract

An exact treatment of the Anderson - Hasegawa two - site model, incorporating the presence of superexchange and polarons, is used to compute the heat capacity. The calculated results point to the dominance of the lattice contribution, especially in the ferromagnetic regime. This behavior is in qualitative agreement with experimental findings.

PACS No. 63.20. Kr, 75.30. Et, 75.40.-s

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The Anderson-Hasegawa (AH) model [1] is a two-site realization of the basic idea of double - exchange (DE) proposed by Zener [2] almost fifty years ago. In the DE scenario a localized spin is visualized to be strongly 'Hund's rule' coupled to an itinerant spin at the same site governed by strength J_H, whereas the itinerant spin can tunnel from site to site accompanied by a 'hopping integral' t. Because of large J_H the itinerant spin is polarized along the localized spin, and as it hops to a neighboring site, it carries with it the memory of its spin polarization, thereby polarizing the neighboring local spin as well. Thus transport is correlated with spin ordering of localized moments, leading to concomitant metal-insulator transition and magnetic ordering.

Since its inception the DE concept has undergone several extensions including a superexchange process yielding antiferromagnetic coupling between localized moments, as well as polaronic modification of hopping. Indeed polaronic contributions are considered to be quite important for thermodynamic properties of a doped magnetic system e.g., $La_{1-x}X_xMnO_3$, ($X = Ba$, Ca, Sr etc). Both thermodynamic and transport phenomena in manganites suggest the importance of polaron formation and the consequent localization of charge carriers [3]. The two - site AH model provides an exactly calculable framework in which some of these ideas can be tested, for evaluating measurable properties of manganites in the wider context of a lattice. Besides it is important to keep track of the quantum nature of the localized spin [4] – for instance, Mn^{4+} is a spin - $\frac{3}{2}$ ion – even though in much of the DE literature the localized moment is viewed as a classical vector. Such an exact quantum treatment of the two-site AH model incorporating the roles of superexchange and polarons, and their contributions to phase diagram and heat capacity, are the subject of this Brief Report. For manganites superexchange interaction is also influenced by Jahn-Teller (JT) coupling [5], which is however not considered here for the sake of simplicity.

With the preceding background to the scope and purpose of the present work we start from the AH model including superexchange for which the Hamiltonian can be written as

$$H_{DE} = -t \sum_{\tau} (c_{1\tau}^{\dagger} c_{2\tau} + h.c.) - J_H \sum_{i=1}^{2} \vec{S}_i . \vec{\sigma}_i + J \vec{S}_1 . \vec{S}_2. \qquad (1)$$

Here $c^{\dagger}_{i\tau}(c_{i\tau})$ is the creation(annihilation) operator of the itinerant electron at site i having spin projection τ, $\vec{S}_i$ is the localized spin, $\vec{\sigma}_i$ is the itinerant spin at site i and J is the strength of the superexchange interaction between neighboring sites. For our case we consider $\mid \vec{S}_i \mid = S$, i.e. the localized spins on all sites are taken to have the same value.

From the *exact* eigenvalue of H_{DE} we may take the large J_H limit by expanding upto $O(1/J_H)$ and write an *effective* Hamiltonian for the two - site one electron case as [6]

$$H_{eff} = -t\frac{(S_0+\frac{1}{2})}{2S+1}(c^{\dagger}_1 c_2 + h.c) + J\vec{S}_1.\vec{S}_2 + \Delta E_J(\hat{n}_1+\hat{n}_2). \tag{2}$$

Here S_0 is the magnitude of the total spin (localized plus itinerant) given by $\mid \vec{S}_1+\vec{S}_2+\vec{\sigma} \mid$, and

$$\Delta E_J = \frac{J}{2}\frac{2S-\bar{S}'}{2S+1}(\bar{S}'+1), \tag{3}$$

where $\bar{S}' = S_0 - 1/2$. The first term in Eq. (2) is the one obtained by Anderson-Hasegawa when the localized spin is treated quantum mechanically. The third term, represented by the number operators $\hat{n}_{1(2)}$ for the itinerant electron, modifies the double-exchange mechanism in the presence of the superexchange interaction given by the second term in Eq. (2). This on-site term, proportional to ΔE_J, we should emphasize, is hitherto not widely considered in the literature, and is a direct consequence of the quantum nature of the localized spin. The spin index τ has been omitted from Eq. (2), for the sake of brevity, as the spin moment of the itinerant electron in any case is parallel to the localized moment, in the $J_H \longrightarrow \infty$ limit.

We now turn our attention to the polaronic effects. The minimal model which reflects lattice carrier interaction on the double-exchange can be introduced by dovetailing the Holstein mechanism on the Anderson-Hasegawa Hamiltonian. Therefore, in the limit of large Hund's rule coupling, we may write a two site, single polaron, Anderson-Hasegawa-Holstein Hamiltonian from Eq. (2) as,

$$H \;=\; H_{eff} + g_1\omega_0\sum_{i=1}^{2} n_i(b_i+b_i^{\dagger}) + g_2\omega_0\left[n_1(b_2+b_2^{\dagger})+n_2(b_1+b_1^{\dagger})\right] + \omega_0\sum_{i=1}^{2} b_i^{\dagger}b_i, \tag{4}$$

where, $g_1(g_2)$ denotes the on-site (intersite) electron-phonon coupling strength. Note that we have considered a single phonon mode for interatomic vibrations of frequency ω_0 for

which b_i and $b_i^\dagger$ are the annihilation and creation operators. The Hamiltonian (4), without the term ΔE_J, has been the subject of exact analytical study for $S = \infty$ and $S = \frac{1}{2}$ cases and a numerical solution for the $S = \frac{3}{2}$ case [7].

We separate out the in-phase mode and the out-of-phase mode by introducing new phonon operators $a = (b_1 + b_2)/\sqrt{2}$ and $d = (b_1 - b_2)/\sqrt{2}$ in the Hamiltonian. The in-phase mode does not couple to the electronic degrees of freedom whereas the out-of-phase mode does, leading to an effective electron - phonon Hamiltonian H_d, given by,

$$H_d = \omega_0 d^\dagger d + \Delta E_J \sum_{i=1}^{2} n_i - t\left(\frac{S_0 + \frac{1}{2}}{2S+1}\right)(c_1^\dagger c_2 + h.c.) + g_- \omega_0 (n_1 - n_2)(d + d^\dagger) + J\vec{S}_1.\vec{S}_2, \quad (5)$$

where $g_- = (g_1 - g_2)/\sqrt{2}$. Following [8] we use a Modified Lang-Firsov (MLF) transformation and obtain,

$$\tilde{H}_d = e^R H_d e^{-R}, \quad (6)$$

where $R = \lambda(n_1 - n_2)(d^\dagger - d)$, λ being a variational parameter related to the displacement of the d oscillator. The basis set is given by $|\pm, N\rangle = \frac{1}{\sqrt{2}}(c_1^\dagger \pm c_2^\dagger)\ |0\rangle_e |N\rangle$, where $|+\rangle$ and $|-\rangle$ are the bonding and the antibonding electronic states and $|N\rangle$ denotes the Nth excited oscillator state within the MLF phonon basis. The diagonal part of the Hamiltonian $\tilde{H}_d$ in the chosen basis is treated as the unperturbed Hamiltonian (H_0) and the remaining part of the Hamiltonian $H_1 = \tilde{H}_d - H_0$, as the perturbation.

The unperturbed ground state is the $|+\rangle|0\rangle$ state and the unperturbed energy, $E_0^{(0)} = \epsilon_p - t_{eff} + J\vec{S}_1.\vec{S}_2$. Where $\epsilon_p = \Delta E_J - \omega_0(2g_- - \lambda)\lambda$ and $t_{eff} = t\ \frac{S_0+\frac{1}{2}}{2S+1}\ \exp(-2\lambda^2)$. However, in the exact quantum limit of core spins, for given values of g_- and J, $E_0^{(0)}$ can have four values corresponding to ferromagnetic (FM), canted 1 (CA1), canted 2 (CA2) and antiferromagnetic (AFM) orientation of the two spins for $|\vec{S}_{12}| = |\vec{S}_1 + \vec{S}_2| = 3, 2, 1, 0$ respectively. Th parameter λ is calculated by minimizing the unperturbed ground state energy [8].

We have evaluated the perturbation correction to the energy upto the sixth order and the wave function upto the fifth order. The convergence of the perturbation series is very good for $t/\omega_0 \leq 1$. Further, to study the effect of an external magnetic field ($\vec{h}$) we include

a term $-\tilde{g}\mu_B(\vec{S_1}+\vec{S_2}).\vec{h}$ to the Hamiltonian in equation (4), $\tilde{g}$ being the Lande g factor. We assume that the external magnetic field is along the direction of $\vec{S}_{12}$ and is expressed in units of $\mu_{eff}(=\tilde{g}\mu_B)$=1.

The ferromagnetic (FM) and antiferromagnetic (AFM) orders are related to $S_{12}(=\mid \vec{S}_1 + \vec{S}_2 \mid) = 3$ and 0, whereas $S_{12} = 2$ and 1 are referred to as canted 1 (CA1) and canted 2 (CA2) states respectively. The Fig. 1 shows the phase diagram for the four possible spin orders for our system, in the g_- vs J plane. To study the polaronic character one calculates the static correlation functions $\langle n_1 u_1\rangle_0$ and $\langle n_1 u_2\rangle_0$, where u_1 and u_2 are the lattice deformations at sites 1 and 2 respectively, produced by an electron at site 1 [8]. The locations of the large polaron region (A) and the small polaron region (B) are indicated in the g_- vs J phase digram (Fig. 1). Different ground states, required for our calculation below, can be located from the phase diagram in Fig. 1. As our phase diagrams are very similar to the ones recently presented by Capone and Ciuchi [7] we henceforth focus only on our new results for the heat capacity.

As mentioned earlier our main emphasis in this Report is on heat capacity based on Eq. (5). Recently, there have been many specific heat measurements of the colossal magnetoresistance (CMR) manganites at low temperatures with and without an external magnetic field [9, 10, 11, 12]. According to experiments the specific heat C_V has contributions from conduction electrons, lattice and spin waves. The low temperature data [10, 12], of many CMR materials, show a temperature dependence of the form $C_V = \gamma T + \beta T^3 + \delta T^{3/2}$, here γ, β and δ are constants. The term γ arises from charge carriers and it is proportional to the density of states at the Fermi level and βT^3 is associated with the lattice contribution, β being related to the Debye temperature. The term $\delta T^{3/2}$ gives the spin wave contribution, where the coefficient δ governs the spin wave stiffness. Okuda et al [9] have estimated the electronic specific heat for $La_{1-x}Sr_xMnO_3$ in the ferromagnetic regime and concluded that the carrier mass-renormalization near the metal-insulator transition at $x = 0.16$ is minimal. They have also observed a decrease in the low temperature C_V in the presence of a magnetic field. Motivated by these observations, we have carried out a calculation of the specific heat,

based on the partition function of the system which, from a cumulant expansion upto the 2nd order, is given by [13],

$$Z(\beta) = Z_0(\beta) exp(\int_0^{\beta} d\beta' \int_0^{\beta'} d\beta'' \langle \tilde{H}_1(\beta') \tilde{H}_1(\beta'') \rangle), \tag{7}$$

where $Z_0(\beta) = Tr(e^{-\beta H_0})$; $\tilde{H}_1(\beta) = e^{\beta H_0} H_1 e^{-\beta H_0}$, and $\beta = \frac{1}{K_B T}$. The expression $\langle\rangle$ denotes the usual canonical averaging. The specific heat is then calculated (in arbitrary units) from the well known relation:

$$C_V = -\frac{d}{dT}(\frac{d}{d\beta} ln Z(\beta)). \tag{8}$$

In the low temperature regime only the zero-and one-phonon states contribute.

As the specific heat has a bearing on fundamental properties of CMR materials it is important to address whether the core spins should be treated classically ($S \to \infty$) or quantum mechanically ($S = \frac{3}{2}$) for its theoretical estimation. The difference in the quantum and classical cases for specific heat, as far as the core spins are concerned, is exemplified in Fig. 2(a) and Fig. 2(b) for FM and AFM cases respectively. Temperature is expressed as $\widetilde{T} = k_B T \omega_0$. The quantum case only allows for discrete values of the relative angle between two core spins, while in the classical case the angle varies continuously. The quantum results evidently yield the correct zero temperature limit.

In the two-site single polaron model we do not have any scope to vary the carrier concentration and probe different magnetic states. But we can identify the FM and AFM states in g_- vs J phase diagram, in which the FM state is stable for lower J values and the AFM ground state is obtained for larger J values. In Fig. 3 we show the $C_V/\widetilde{T}$ vs $\widetilde{T}^2$ curves for the FM and AFM cases. It is evident that in the FM case T^3 behavior of specific heat is more pronounced which is in qualitative agreement with the results of [10, 11]. As the stiffness coefficient δ is proportional to J [14], the spin wave contribution is not significant in FM limits. However in the AFM limit ($J = 0.2$) the variation of $C_V/\widetilde{T}$ deviates from the T^3 law and the spin wave contribution is non negligible. These findings are in qualitative agreement with the measurements of Smolyaninova et al [11]. Moreover the magnitude of

$C_V/\widetilde{T}$ for the AFM limit is higher than that in the FM limit, as in Smolyaninova et al[11]. The suppression of C_V in the FM regime can be intuitively ascribed to the absence of spin wave fluctuations, as mentioned earlier. However, while calculating heat capacity in $S \to \infty$ limit it can be shown that spin wave contribution (i.e. $C_V \propto \widetilde{T}^{3/2}$) is dominant in FM case. This is due to averaging over all possible relative orientations of core spins.

We show in Fig. 4 the variation of the specific heat in the low temperature region in the FM state with zero and one phonon states. With application of an external magnetic field $\vec{h}$, C_V takes lower values than for $\vec{h} = 0$ which is expected, as the average energy decreases with application of $\vec{h}$ in the FM state. For CA1($\mid \vec{S}_{12} \mid = 2$), CA2($\mid \vec{S}_{12} \mid = 1$) and AFM ($\mid \vec{S}_{12} \mid = 0$) states the external magnetic field will tend to align the core spins to ferromagnetic order($\mid \vec{S}_{12} \mid = 3$). For CA1, CA2 and AFM states at low field and low temperatures it can be shown from the present calculation that C_V increases from the $\vec{h} = 0$ limit as long as $\vec{h}$ does not shift $\mid \vec{S}_{12} \mid$ to higher values. For larger $\vec{h}$, as the ground state changes from lower $\mid \vec{S}_{12} \mid$ to higher ones, C_V decreases in the low temperature region. For CMR materials, there are some reports on measurements of field dependence of C_V in the FM state [9] and also in the half doped case [11]. It was found that for low doping regions, C_V decreases with an increasing magnetic field [9]. However the half doped material showed C_V/T as independent of applied field [11]. The present calculation of the external magnetic field dependence of C_V qualitatively agrees with these experimental findings in the FM limit.

In conclusion, the present calculation of C_V using an exactly solvable model reveals some of the important features of the double exchange polaronic system. The discreteness associated with the effective hopping as a result of the quantum nature of the local spin was shown to have a significant consequence for thermodynamic properties. As analytic calculations of the heat capacity for CMR material to fit experimental results are not starightforward, because of the involvement of several parameters, the present calculation for a simplified model indeed serves an important role in indicating general trends. Further, a comparison of the computed C_V with measured values underscores the importance of the quantum nature of the local spin, a fact often ignored in the current CMR literature.

We are grateful to Sashi Satpathy for discussion on the polaronic mechanism. SD wishes to thank S. D. Mahanti for generating interest in manganites.

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Figure Captions :

FIG. 1. The g_- vs J phase diagram ($\vec{h} = 0$) for $\mid \vec{S}_1 \mid = \mid \vec{S}_2 \mid = \frac{3}{2}$, $t = 1$ and $\omega_0 = 1$. (**A**) and (**B**) denote large polaron and small polaron region respectively.

FIG. 2. Variations of C_V (in arbitrary units) with temperature $\widetilde{T}(= k_B T\omega_0)$ for $h = 0$, $t = 1$, $\omega_0 = 1$, in classical (solid line) and quantum (dashed line) formulations of the core spins for (a) FM ground state($g_- = 0.2$, $J = 0.02$) and (b) AFM ground state ($g_- = 0.6$, $J = 0.2$).

FIG. 3. $C_V/\widetilde{T}$ vs $\widetilde{T}^2$ for $h = 0$, $t = 1$, $\omega_0 = 1$ in (a) FM ground state and (b) AFM ground state for facilitating comparison with experiments. Here C_V is in arbitrary unit and $\widetilde{T} = k_B T\omega_0$. The results of Fig. 3(a) are in qualitative agreement with Fig. 2 of Hamilton et al [10].

FIG. 4. Variations of C_V (in arbitrary units) for $g_- = 0.6$, $J = 0.01$ and $t = 1$, $\omega_0 = 1$, for different values of the magnetic field $h = 0$, 0.01, 0.05, which exemplify the magnetic field dependence of C_V.

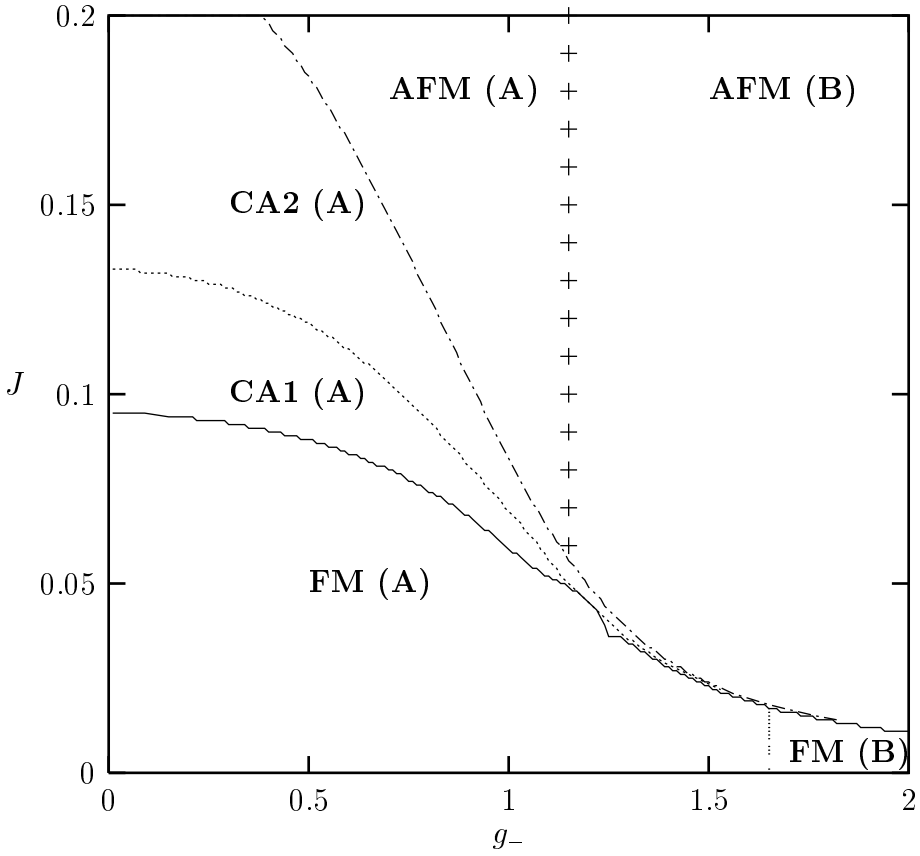


FIG. 1

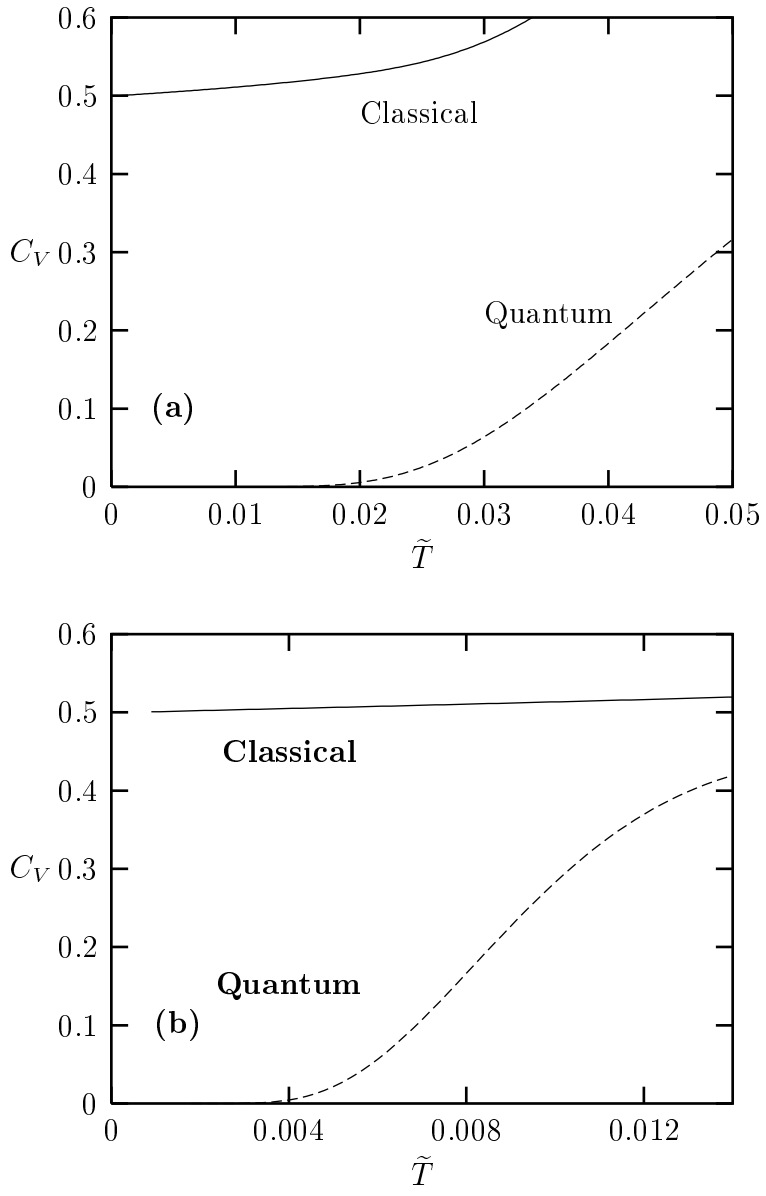
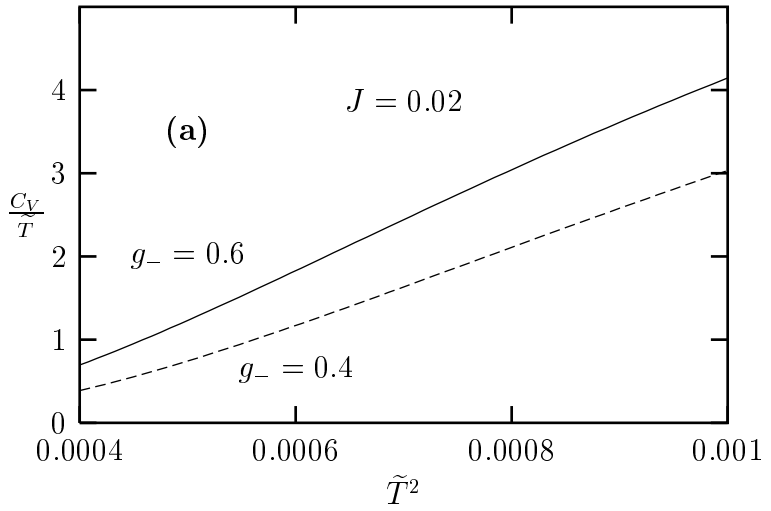

0.6
0.5
0.4
C_V 0.3
0.2
0.1
0
Classical
Quantum
(a)
0
0.01
0.02
0.03
0.04
0.05
$\widetilde{T}$
0.6
0.5
0.4
C_V 0.3
0.2
0.1
0
Classical
Quantum
(b)
0
0.004
0.008
0.012
$\widetilde{T}$

FIG. 2


4
3
2
1
0
$\frac{C_V}{\widetilde{T}}$
(a)
$J = 0.02$
$g_- = 0.6$
$g_- = 0.4$
0.0004
0.0006
0.0008
0.001
$\widetilde{T}^2$

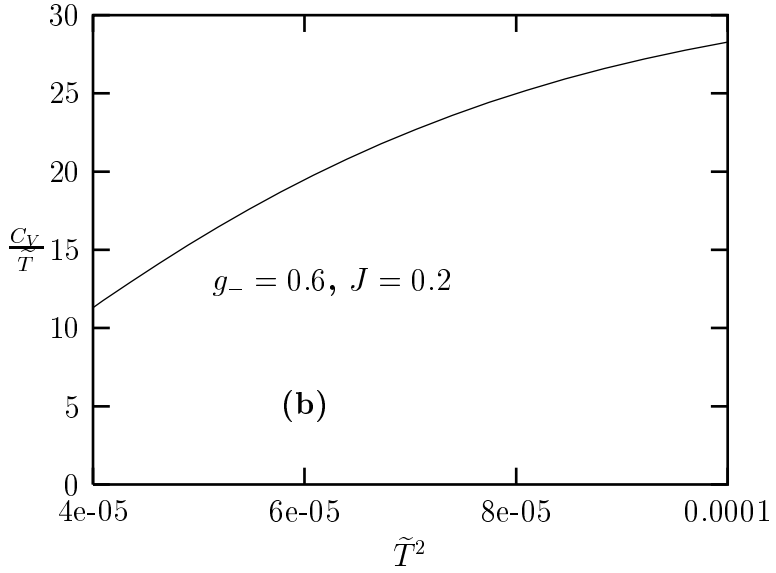

30
25
20
15
10
5
0
$\frac{C_V}{\widetilde{T}}$
$g_- = 0.6$, $J = 0.2$
(b)
4e-05
6e-05
8e-05
0.0001
$\widetilde{T}^2$

FIG. 3

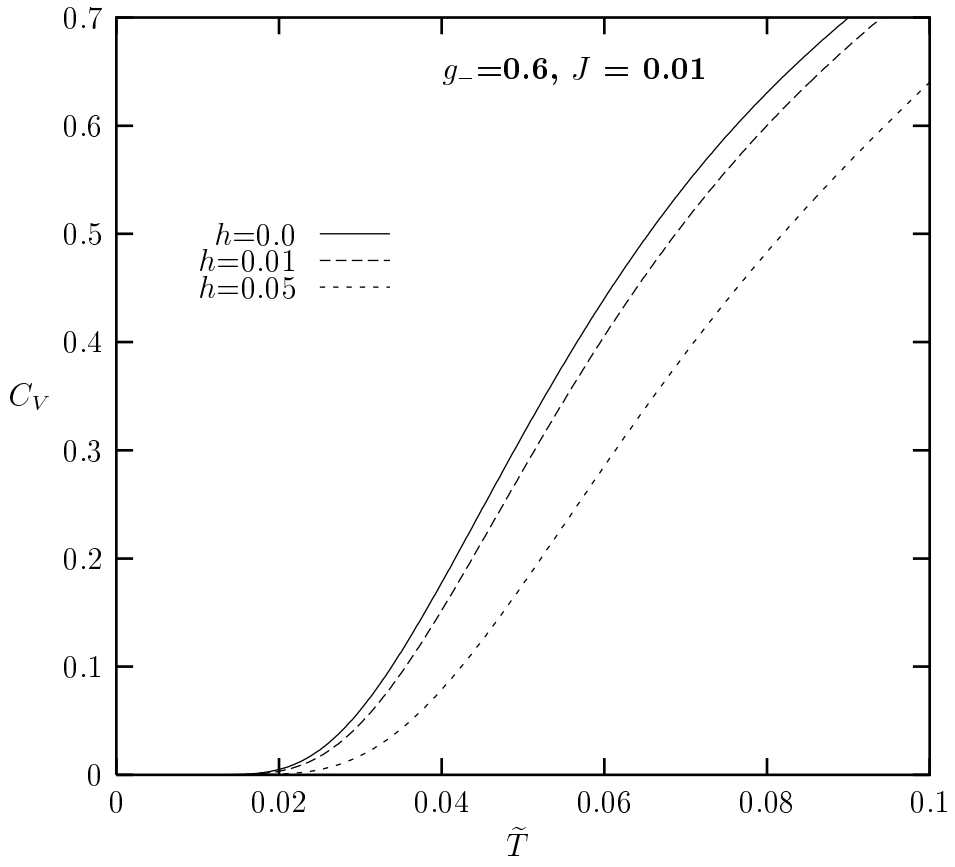

g_-=0.6, J = 0.01
h=0.0
h=0.01
h=0.05
C_V
$\widetilde{T}$
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.02
0.04
0.06
0.08
0.1

FIG. 4