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Thermodynamic signatures of geometrical frustration in clusters

R C Juliano[1], E G Santos[2] and M A Gusmão[1]

[1] Instituto de Física, Universidade Federal do Rio Grande do Sul, CP 15051, 91501-970 Porto Alegre, RS, Brazil
[2] Universidade Federal do Pampa, Campus Alegrete, Avenida Tiaraju 810, 97546-550 Alegrete, RS, Brazil

E-mail: miguel.gusmao@ufrgs.br

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Abstract

We develop a comparative study of the extended Hubbard model on three-site clusters of triangular and linear geometries, searching for geometrical-frustration effects on thermodynamic properties. Using exact diagonalization, we evaluate physical quantities such as specific heat, entropy, and spin correlations as functions of temperature, varying interaction parameters and electron density. In particular, we highlight the existence of clear signatures of frustration in the thermal behavior of the electronic specific heat in triangular clusters, which allows us to suggest that specific-heat measurements may be an important experimental tool to detect geometrical frustration in correlated-electron systems.

Keywords: Hubbard model, geometrical frustration, thermodynamic properties

(Some figures may appear in colour only in the online journal)

1. Introduction

Geometrical frustration of magnetic order has been a long-standing research subject of great interest [1]. Experimentally, many compounds have been investigated, including three-dimensional (3D) pyrochlores [2], and quasi-two-dimensional compounds containing planar structures generally identifiable as triangular or kagomé lattices [3–5].

From the theoretical point of view, starting with localized-spin models, the absence of long-range magnetic order and the appearance of a spin-liquid ground-state are well-established features [1]. Allowing for charge degrees of freedom, the standard Hubbard model [6], with a local Coulomb repulsion U and nearest neighbor hopping is the natural choice, but the theoretical complexity is substantially augmented. For bipartite lattices at half filling (one electron per site) it is well known that the ground-state is antiferromagnetic (AF), approaching the Heisenberg limit at large-U. This is well described, for example, by dynamical mean field theory (DMFT) [7], which employs a purely local self-energy to evaluate single-particle Green's functions. However, DMFT cannot account for inter-site correlations, which must be taken into account if one wants to look for geometrical-frustration effects. So, the relevant minimal unit is not a single site but a triangular cluster, the smallest structure that shows magnetic frustration. Many methods have been proposed in the literature [8–11] to use clusters as building blocks for lattices. Some applications for frustrated planar structures like the kagomé and triangular lattices have been reported [12, 13], but the amount of clear-cut results is still small. One of the main difficulties in going from triangular clusters to lattices lies in the fact that the above mentioned two-dimensional (2D) lattices present flat bands and/or van Hove singularities in the uncorrelated density of states (DOS). Correlations tend to mix these singular parts with the smooth ones, even more if a Mott gap opens up in the strong-coupling regime where geometrical frustration plays a role. Consequently, the chemical potential often falls in a region of strongly varying DOS, which is not a friendly situation for numerical methods.

Here, instead of attempting to develop connected-cluster approximations, we investigate in detail what happens inside a single cluster, aiming to detect signatures of geometrical frustration. To this purpose, we compare exact-diagonalization results for three-site clusters in triangular and linear geometries. We focus on thermodynamic properties, particularly the specific heat, which tends to show already in small clusters the overall behavior observed in lattice systems. A characteristic feature of the Hubbard model is a two-peak structure of the

electronic specific heat as a function of temperature [7, 14–17]. Our main finding is a significant difference in this two-peak structure when we compare frustrated (triangular) and non-frustrated (linear) geometries. A reduction of the low-temperature spin-excitation peak is observed in the presence of geometrical frustration, essentially with no effect on the high-T charge peak. This reduction is suppressed by doping away from half-filling in the frustrated cluster, but no important changes occur in the non-frustrated one. These results suggest that specific-heat measurements may be an important tool to detect geometrical-frustration effects in correlated-electron systems.

Complementary to the specific-heat results, we study the temperature behavior of spin correlations for various interaction regimes. We also include a nearest-neighbor repulsion V in order to investigate its effect on frustration-related properties. It should be noted that such a non-local interaction introduces further difficulties to the lattice problem since it is not restricted to a cluster. This implies that cluster connections are no longer associated to hopping only, as supposed, for instance, by DMFT. Therefore, an evaluation of the importance of inter-site interaction at the cluster level is of high relevance.

2. Model and method

We use a cluster version of the extended Hubbard model with local (U) and nearest-neighbor (V) Coulomb interactions. It is defined by the Hamiltonian

$$H = -t\sum_{\langle ij\rangle\sigma}\left(c^{\dagger}_{i\sigma}c_{j\sigma} + c^{\dagger}_{j\sigma}c_{i\sigma}\right) + U\sum_{i} n_{i\uparrow}n_{i\downarrow} + V\sum_{\langle ij\rangle} n_i n_j, \tag{1}$$

where we employ the usual notation for creation, annihilation, and number operators in the Wannier representation, $i = 1, 2, 3$ labels the sites of a cluster of triangular or linear geometry with $\langle ij\rangle$ indicating nearest-neighbor pairs, σ refers to spin states (*up* or *down*), $n_i = n_{i\uparrow} + n_{i\downarrow}$, and t is the hopping parameter. We adopt a units system in which Boltzmann's constant k_B and Planck's constant $\hbar$ are omitted, implying that energy and temperature have the same unit, and spins are dimensionless variables.

Previous studies of the triangular-cluster Hubbard model [18, 19] showed the appearance of noncollinear spin ordering when using an unrestricted Hartree–Fock approximation. Since we are interested in investigating spin frustration, we must resort to exact diagonalization. A convenient basis for a matrix representation of H is provided by the energy eigenstates for $t = V = 0$. They are obtained from the particle vacuum by the usual construction of Fock-space Wannier states, applying products of creation operators $c^{\dagger}_{i\sigma}$ with the appropriate site and spin subscripts and in a well defined order. Thus, each basis state specifies number and spin states of electrons at each site, which are organized by total number of particles (N) and by a component (S^z_T) of the total spin.

Exact diagonalization of the Hamiltonian matrix of a three-site cluster gives us a set of energy eigenvalues and corresponding eigenvectors. The single-particle eigenvalues ($E_{1,\alpha}$) are easily found analytically, with the results

$$\begin{aligned} E^T_{1,1} &= -2t, \quad E^T_{1,2} = E^T_{1,3} = t, \\ E^L_{1,1} &= -\sqrt{2}t, \quad E^L_{1,2} = 0, \quad E^L_{1,3} = \sqrt{2}t, \end{aligned} \tag{2}$$

respectively for the triangular (T) and linear (L) clusters. The empty- ($N = 0$) and full-cluster ($N = 6$) problems are trivial, and some subspaces are related by particle-hole transformation. Detailed analyses of the energy spectrum and various physical properties of these kind of clusters (as well as other geometries) have been reported in the literature [20–26], either for the same model considered here or variants including other terms, like spin–spin coupling or external fields. In some of these previous works analytical expressions of energy eigenvalues are obtained. For our purposes, it is more convenient to numerically diagonalize the full 64×64 Hamiltonian matrix for all possible occupations, even though it is built up as block-diagonal in N and S^z_T. Upon diagonalization, the energy eigenvalues yield the cluster partition function and density matrix in the energy representation, while the eigenvectors provide the transformation matrix that relates this representation to the original basis. Then, besides global thermodynamic quantities like average energy and entropy, evaluation of site-dependent ones, as double-occupancy or spin correlations, can be readily performed.

Some differences are observed depending on whether we fix the particle number (canonical ensemble) or its average value by adjusting a chemical potential (grand canonical ensemble). We will show results for both cases, with comments on the differences when relevant. It is arguable which one is best suited to apply to clusters if one wants to make comparisons with real systems. It is certainly simpler to work with a fixed number of particles for numerical calculations, but it is mandatory to adjust the chemical potential, for instance, to investigate doping effects by imposing fractional filling factors.

3. Thermodynamic properties

3.1. Specific heat

We evaluate the electronic specific heat (C) through a numerical derivative of the average energy per particle with respect to temperature. Examples are presented in figure 2, which shows plots of specific heat as a function of temperature for some representative values of U, in the half-filling case (number of electrons fixed at $N = 3$). We keep $V = 0$ for now, and discuss the effects of inter-site interaction later on.

For large U, a two-peak structure characteristic of strongly correlated systems is observed. As the strength of the Coulomb interaction increases, the initial single peak centered at $T \sim t$, reflecting charge excitations, moves to higher temperatures, while a low-T spin-excitation peak appears. This can be understood by inspecting the behavior of energy eigenvalues

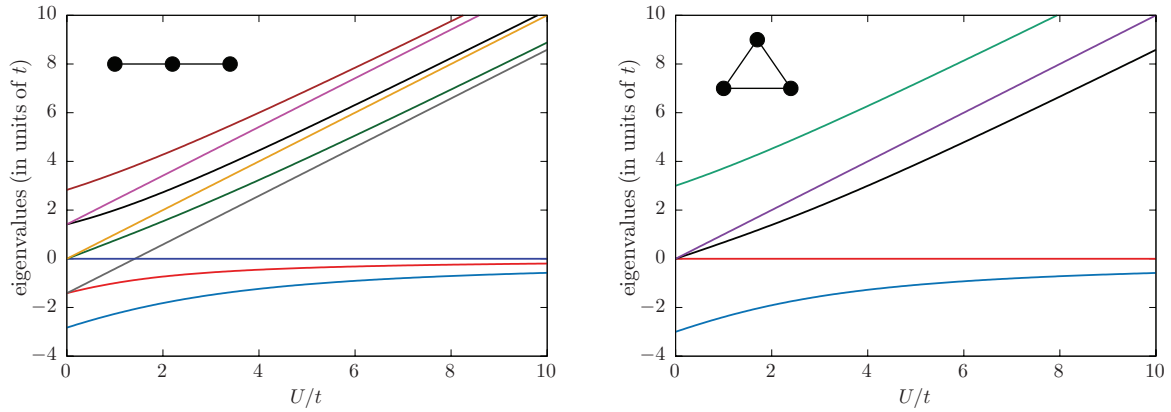

Figure 1. Dependence of energy eigenvalues on the local interaction U (with $V = 0$) for three electrons on three-site clusters of linear and triangular geometries. The horizontal lines correspond to states with the spin eigenvalue $S = 3/2$ (degeneracy 4). The remaining lines are for states with $S = 1/2$, with additional degeneracy (also amounting to 4) in the triangle due to the equivalence of all sites.

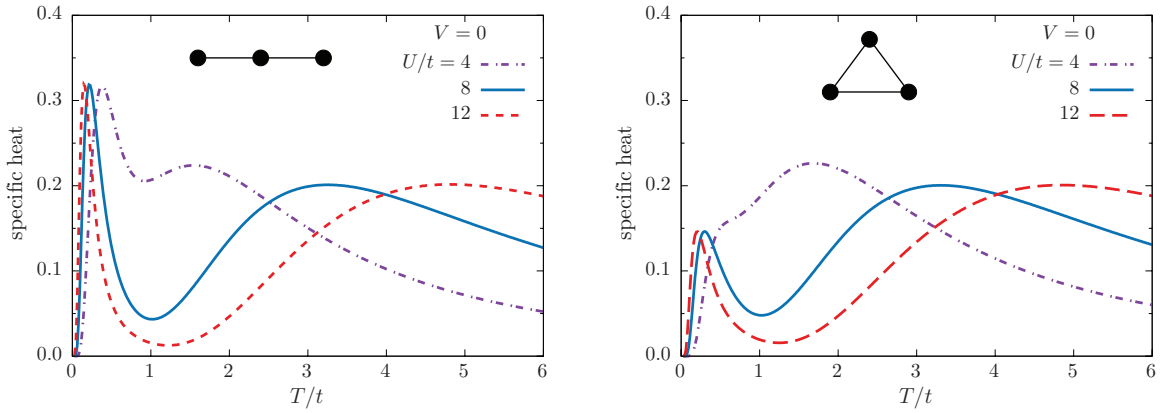

Figure 2. Behavior of the electronic specific heat with temperature, for the quoted values of the Coulomb interaction U, in half-filled isolated three-site clusters of linear and triangular geometries.

with U, figure 1. At small U, all the excited states are close in energy, and at a distance to the ground-state that is consistent with the broad high-temperature peak of $C(T)$. In the large-U region, the $S = 1/2$ ground-state subspace lies close to the first-excited triplet of $S = 3/2$, and does not change much with U. Thus, low-energy spin excitations are easily generated, yielding the small peak that becomes detached from the main one as the energies of the other states grow with U.

From the above comments, it is clear that the low-temperature specific-heat peak can be recognized as Schottky-type [27]. In particular, the peak heights at large U for the triangular cluster are in very good agreement with the general results for a two-level system using table 1 of [27]. The temperatures of the maxima are also reproduced using the obtained gap between the two states involved. The agreement is not so good for the linear cluster due to the existence of a pair of exited levels very close in energy in the large-U limit. In this case, a rough estimation considering them as a single level, with added degeneracies and an average gap, still gives fairly consistent values for the position and height of the low-T peak.

It is also worth mentioning that in the large-U limit, and at low temperatures, where charge fluctuations are essentially frozen, the specific-heat behavior that we obtain reduces to that of the spin-1/2 Heisenberg model, as expected. For instance, our low-temperature peak reproduces the $C(T)$ curve for the Heisenberg model in a triangle reported by Isoda [28], provided that we reescale the temperature axis to have it in units of the exchange coupling J, here given by t^2/U.

We wish to point out the striking difference in intensity of the low-temperature peaks when we compare linear and triangular clusters in figure 2. The linear-cluster peaks resemble much more closely what is obtained, for instance, in DMFT [7] or in a two-site cluster [22], with the narrow low-T peak higher than the broad high-T one. We interpret a reduced spin peak as indicative of spin frustration in the triangular geometry. In fact, this difference in specific-heat behavior can be directly correlated to the ground-state entropies of the two clusters, as we have seen in the discussion of the Schottky nature of the first peak. As shown in figure 1, the triangular geometry presents a ground-state degeneracy equal to 4, twice as large as that of the linear case. This shows up in the zero-temperature residual entropy, which in this case is correspondingly twice as large, as can be seen in figure 3. An interesting feature of these entropy results is the nearly perfectly defined crossing points of all curves. The existence of such points in the evolution of thermodynamic quantities as functions of some parameter has been largely discussed in the literature [29, 30].

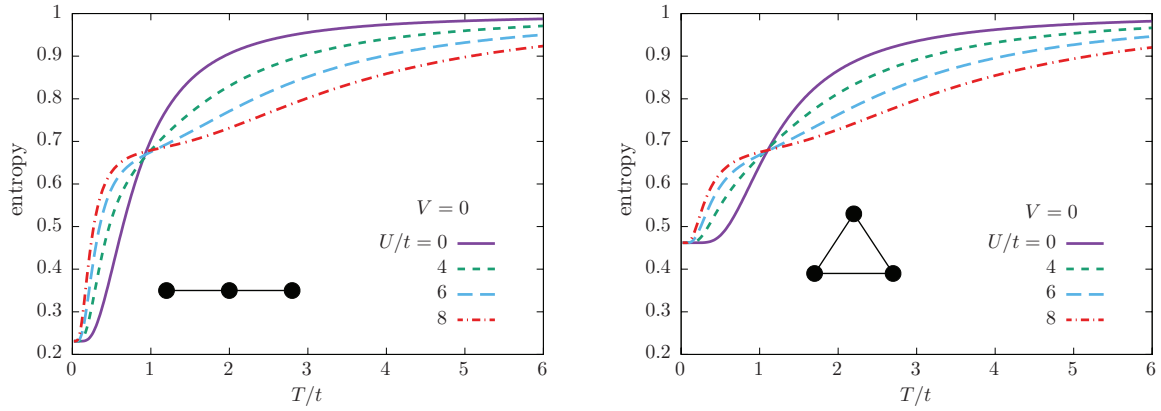

Figure 3. Entropy versus temperature for both cluster geometries. Note the difference in residual entropy between the two cases, as well as the existence of crossing points between the low- and high-temperature regions.

Here, it is quite clear that they mark a crossover between spin and charge excitations as the temperature rises.

The entropy results of figure 3 were obtained for isolated clusters. Although the overall shape of the curves is similar, no crossing point is seen with calculations performed using the grand canonical ensemble. This is probably due to additional (uncorrelated) charge fluctuations that are introduced in this case. For the same reason, differences on the entropy curves appear at low temperatures for certain values of U. In particular, a higher residual entropy is observed for $U = 0$ in the open triangular cluster, shown in figure 4, reflecting a near coincidence of the lowest grand canonical eigenvalues $(E - \mu N)$ for 2, 3, and 4 particles as $T \to 0$ when the chemical potential μ is adjusted to an average occupation number $\langle N \rangle = 3$.

As a further check that geometrical frustration is associated to the reduced low-T specific-heat peak in triangular clusters, we studied the effect of doping away from half-filling. Figure 5 shows that changes in occupation number have little effect on the low-T peak in the linear cluster, while a fast growth of this peak is observed in the triangle as the amount of doping increases. As mentioned before, in order to choose fractional site occupations we must use the grand canonical ensemble. An observed side effect is that the broad maximum of the specific heat for $n = 1$ is substantially higher in comparison to the isolated cluster (figure 2), which once more can be attributed to particle-number fluctuations. In contrast, in the absence of doping the low-T peaks are essentially equal in isolated and open clusters for each geometry.

3.2. Spin correlations

Investigating spin correlations is a necessary complement of our study of geometrical-frustration effects. Due to the absence of spin anisotropies or magnetic order, we may focus on a single spin component, evaluating the average $\langle S_i^z S_j^z \rangle$ for two distinct sites of a cluster. All pairs of sites are equivalent in the triangle, while center-border and border-border correlations should be different in the linear three-site cluster. The calculation is straightforward since our basis states are eigenvectors of S_i^z.

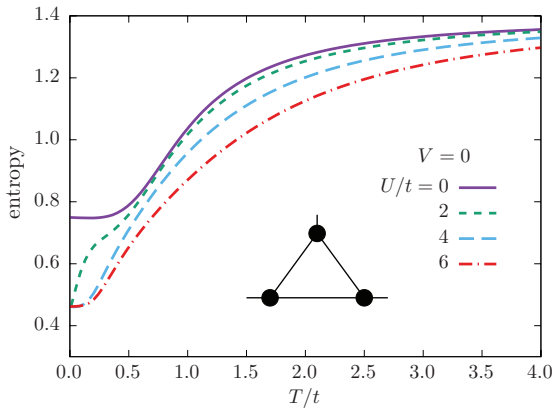

Figure 4. Entropy versus temperature for the triangular cluster in the grand canonical ensemble with average occupation $\langle N \rangle = 3$. A higher residual entropy for $U = 0$ is clearly seen, as discussed in the text. Also noticeable is that a well defined crossing point between the low- and high-temperature regions no longer exists.

Typical results are presented in figure 6. It can be seen that reasonably strong AF correlations exist between border and center sites in the linear cluster, while the two border sites are ferromagnetically correlated. This correlation pattern is consistent with a tendency to AF ordering, which is easily understood by the usual exchange mechanism, with virtual hopping processes allowed between neighboring singly occupied sites only if the electrons have opposite spins. By the same mechanism, but with different result, correlations in the triangular cluster are always AF, and their substantially lower values are indicative of geometrical frustration of nearest-neighbor AF interactions. As U increases, the zero-temperature limit approaches the exact Heisenberg value on the triangle [12], $\langle S_i^z S_j^z \rangle = -1/12$. The results shown in figure 6 have been generated for open clusters, but we checked that the outcome of calculations for isolated clusters do not show any significant differences.

3.3. Effect of inter-site interaction

We now turn to a brief discussion of how the results that we have shown up to here are affected by a nonzero inter-site

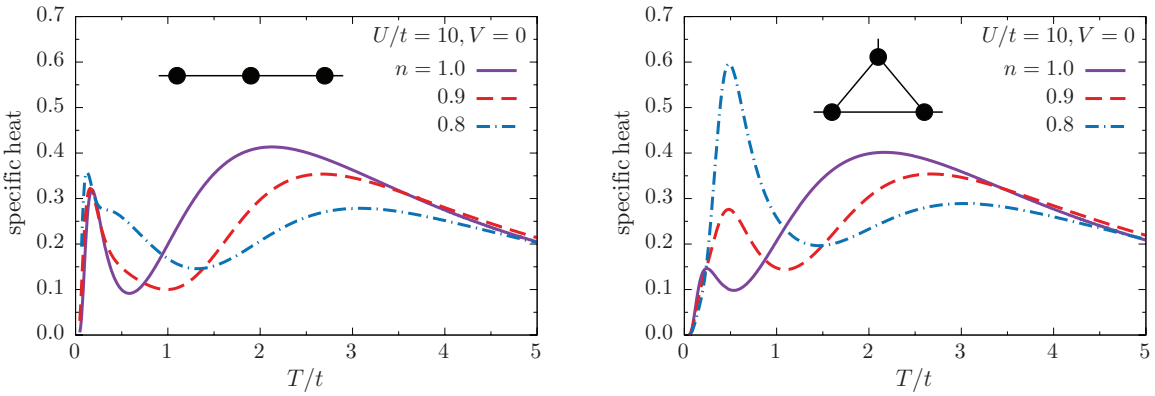

Figure 5. Comparison of the effect of doping ($n = 0.9$ and 0.8 electrons per site) on the electronic specific heat of three-site clusters of linear and triangular geometries. Short dangling lines on the clusters indicate that they are not isolated.

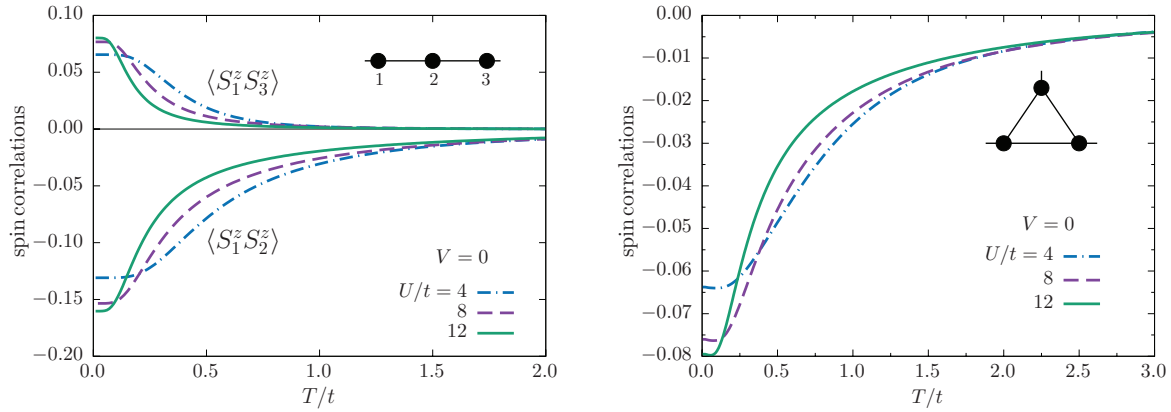

Figure 6. Variation of spin correlations with temperature for both geometries and the quoted values of U. For the linear geometry we number the sites and indicate which correlation corresponds to each set of curves. Note the difference in scale and range of correlations between the two plots.

Coulomb repulsion V. For a small ratio V/U, we mainly see an effective reduction of the on-site interaction. By increasing the energy of configurations with electrons on nearest-neighbor sites, V reduces the penalty for double occupation, which is similar to having a weaker on-site repulsion U. We exemplify with the thermal behavior of the specific-heat of an isolated triangular cluster in figure 7, where we see that the charge-excitation peak is displaced to lower temperatures, eventually merging with the spin peak. Similar results are obtained for the linear cluster.

This low-V effect is what should be mostly observed in real systems. However, from a theoretical point of view, we can explore more freely the parameter space, even considering a region of dominant inter-site interaction in which we would have the formation of local *doublons*, which have been object of some investigation, mainly with focus on dynamic properties [31, 32]. Similarly to what we discussed for spins with large U, in bipartite lattices at half filling a large V should yield charge-density order, with alternating doublons and empty sites (*holons*). But one could argue that this kind of order should also be frustrated in triangular-based structures. In a single three-site cluster with an average of one electron per site we can have at most one doublon, one holon, and a single spin. Nevertheless, the difference between linear and triangular clusters shows up in the fraction of doubly occupied

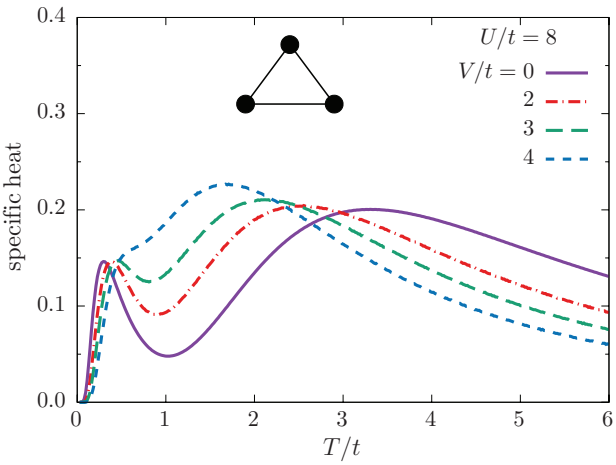

Figure 7. Effect of the inter-site interaction V for a large value of U in the isolated triangular cluster at half filling.

sites, as shown in figure 8, where we see that there is a larger stability region of the doublon (density close to 1/3) in the linear trimer. This is easily understood by the fact that a doublon and a single electron can stay at the border sites, leaving the middle site empty, while the inter-site repulsion V cannot be avoided in a triangular geometry. Obviously the complexity increases if these simple units are connected to form a lattice,

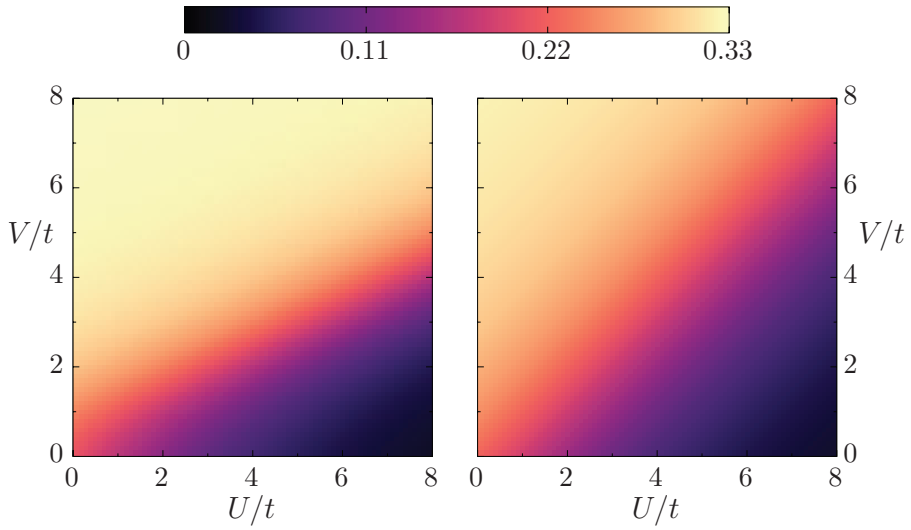

Figure 8. Fraction of doubly occupied sites (color scale) on linear (left) and triangular (right) three-site clusters, in the low-temperature regime ($T = 0.1\,t$), for local and nearest-neighbor couplings U and V varying over a wide range.

with V acting also as inter-cluster interaction, and electron motion not restricted to a single cluster.

4. Conclusions

With focus on geometrical-frustration effects, we have performed a detailed study of some thermodynamic properties of the extended Hubbard model on three-site clusters. In general lines, this investigation was conducted through of a comparative analysis of exact-diagonalization results for clusters of triangular and linear geometries. Our main finding refers to the thermal behavior of the electronic specific heat in a regime of strong on-site interaction U. Besides reproducing the overall two-peak structure also seen in lattice models and real systems, we found that in the triangular geometry there is a significant reduction of the low-temperature peak, associated to spin degrees of freedom. Our interpretation of this feature as indicative of geometrical frustration is based on its suppression by doping away from half-filling as well as its absence in the linear cluster. On the other hand, even though in a probably unrealistic regime ($U < V$), our analysis of the interplay between local and non-local interactions yielded the interesting suggestion that charge (instead of spin) order could also be geometrically frustrated.

Going back to the large-U behavior of the specific heat, which we consider to be our most important result, we were able to relate the reduced low-T peak to a higher ground-state entropy associated to the cluster geometry, which is consistent with the identification of this peak as Schottky-type. Even though we presented results for a cluster, a large residual entropy is recognized as a distinctive property of frustrated-lattice phases such as the spin liquid. We should thus expect the same kind of specific-heat behavior in real systems.

The above results point to the possibility of using specific-heat measurements as a probe of geometrical frustration. Incidentally, it is worth remarking that a reduction of the spin peak might be overlooked in experiments since it is usual to plot the ratio C/T, consequently enhancing low-T values. Another experimental issue is that 2D frustrated structures in real materials are not isolated but actually exist inside 3D compounds, characterizing quasi-2D systems. In this case, weak interplane coupling usually yields ordered phases at very low temperatures, and a sharp peak in the specific heat is associated to the ordering transition [33]. 2D geometrical-frustration effects would then be observed only above this transition temperature, provided it was low enough to allow such effects to be still visible. On the other hand, it is also possible that a sufficiently strong 2D frustration prevented the ultimate 3D ordering. Hopefully, all of these interesting scenarios will eventually be found in new materials.

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ORCID iDs

M A Gusmão https://orcid.org/0000-0003-2007-1597

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