

Theoretical study of the effect of temperature on the magnetism of transition metal clusters

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Abstract. – The temperature effects on the magnetic properties of transition metal clusters are investigated by computer simulations which combine the classical potential approximation with the generalization of our recently proposed tight-binding molecular-dynamics method that includes explicit incorporation of spin-orbit interactions and spin fluctuations. The efficacy of this new method is demonstrated by application to small and intermediate size Ni_n-clusters ($n \leq 201$) for which experimental data are available for comparison. The results obtained are in good agreement with the recent experimental findings.

Zero-temperature (ZT) model approximations have been found to be adequate in verifying the earlier experimentally measured magnetic moments (MMs) reported for small 3d-transition metal (TM) clusters (see, for example, ref. [1] and references therein). A number of computational approaches ranging from *ab initio* [2] to semi-empirical tight-binding (TB) approximations [3, 4] valid at ZT have been proposed since then. The central assumption of these approaches is that the cluster is a single-domain particle in which the spin magnetic moments (SMMs) of the cluster atoms are aligned along the same direction, *i.e.*, they are collinear. Furthermore, all these approaches almost always ignore the contribution of orbital magnetic moment (OMM) to the MM of the cluster [2, 5]. As a result, the MM of each cluster atom-*i* is assumed to derive entirely from the spin of the electrons and obtained from the formula $\mu_i = n_{i+} - n_{i-}$, where n_{i+} (n_{i-}) denotes the number of electrons with spin-up (spin-down) in the *i*-th cluster atom.

New experimental results, however, have shown the existing ZT models to be inadequate in describing many of the observed behaviors and have provided a challenge to the theories

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to explicitly incorporate finite temperature and spin-orbit effects accurately for a correct description [6–8]. These new experimental results pertain to: The magnetic phase transitions, the variation of the cluster-MMs with temperature, or the variation of the cluster-Curie (T_C^{cl}), and Debye (Θ_D^{cl}) temperature with the cluster size and the way T_C^{cl} and Θ_D^{cl} converge to their bulk phase counterparts (T_C^{bulk} and Θ_D^{bulk}) respectively.

The evolution of a ZT formalism to a finite-temperature (FT) approach involves the following basic steps: i) The replacement of the collinear aspect of the ZT-theories. ii) To allow for a statistical thermodynamic averaging of low-energy lying cluster states with random spin and structural configurations as these are dictated by the temperature. Thus, the problem may be approached in two steps. In the first, the non-collinearity effects (see ref. [9]) are included followed by the temperature ones.

In the present letter, we present such a description by generalizing our ZT symmetry and spin unrestricted tight-binding molecular-dynamics (TBMD) formalism [10]. We first introduce the main interactions responsible for spin redistributions followed by the incorporation of temperature effects. We then demonstrate the applicability of the new formalism by investigating the variation with temperature of the magnetic properties of small Ni clusters and compare with the new experimental results on these systems.

Incorporation of non-collinear effects. – We generalize our well-tested ZT TBMD approach at the Hubbard- U level of approximation [10] to include the non-collinear cluster magnetism. In the original ZT TBMD model an exchange-splitting parameter $s_0^{(i)}$ was introduced which is proportional to the intra-site Coulomb interaction U and specifies the energy splitting between spin-up and spin-down electrons in the i -th atom in accordance with results obtained by *ab initio* methods. Thus, within this model, a site-diagonal spin-dependent Hamiltonian term $\mathbf{V}_{spin}^{(i)}$ is introduced of the form

$$\mathbf{V}_{spin}^{(i)} = \begin{pmatrix} s_0^{(i)} & 0 \\ 0 & -s_0^{(i)} \end{pmatrix}. \quad (1)$$

The model described by eq. (1), assumes collinear alignment of the MMs of the cluster atoms; the former assumed collinear to the z -axis of a local xyz -system assigned to the i -th cluster atom. In generalizing this model, it is assumed that the deviation of the direction of the MM μ_i of the i -th cluster atom from the Z -axis of the global coordinate system XYZ is specified by the polar angles (θ_i, ϕ_i) defined with respect to this XYZ system. As a result, the potential $\mathbf{V}_{spin}^{(i)}$, originally defined with respect to the local coordinate system xyz of the i -th atom, is transformed into its expression $\mathbf{V}_{spin}^{(i),global}$ in the global system XYZ as follows [11,12]:

$$\mathbf{V}_{spin}^{(i),global} = \Xi^\dagger(\theta_i, \phi_i) \mathbf{V}_{spin}^{(i)} \Xi(\theta_i, \phi_i), \quad (2)$$

where $\Xi(\theta_i, \phi_i)$ is the standard spin- $\frac{1}{2}$ -rotation matrix:

$$\Xi(\theta_i, \phi_i) = \begin{pmatrix} e^{i\phi_i/2} \cos \theta_i/2 & e^{-i\phi_i/2} \sin \theta_i/2 \\ -e^{i\phi_i/2} \sin \theta_i/2 & e^{-i\phi_i/2} \cos \theta_i/2 \end{pmatrix}. \quad (3)$$

It is assumed that the Z -axis of the global system can be arbitrarily chosen and the obvious choice is to take Z in alignment with the easy axis of the system.

Within the above description we introduce the Spin-Orbit interaction, $V_{SO}^{(i)}$, in the i -th atom within the $\mathbf{L} \cdot \mathbf{S}$ coupling scheme, *i.e.*, $V_{SO}^{(i)} = -\lambda^{(i)} \mathbf{L}^{(i)} \cdot \mathbf{S}^{(i)}$, where $\lambda^{(i)}$ is the spin-orbit

coupling constant for the i -th atom, $\mathbf{L}^{(i)}$ its orbital angular momentum along the Z -axis and $\mathbf{S}^{(i)}$ its total spin in the direction of μ_i [13].

In an alternative formulation within the Hubbard- U model approximation to the e - e correlations the spin-mixing interaction may be derived from a Coulomb-type Hamiltonian term of the form [3, 4]: $\mathbf{V}_{smix} = -U \sum_{l\sigma} \rho_{l\sigma, l\bar{\sigma}} c_{l\bar{\sigma}}^\dagger c_{l\sigma}$, where $c_{l\sigma}^\dagger$ ($c_{l\sigma}$) is the creation (annihilation) operator for an electron with spin σ at site l and $\rho_{l\bar{\sigma}, l\sigma}$ denote the electron density matrix elements *i.e.*, $\rho_{l\sigma, l\bar{\sigma}} = \langle c_{l\bar{\sigma}}^\dagger c_{l\sigma} \rangle$. It can be easily verified that the Hamiltonian term \mathbf{V}_{smix} is equivalent to that given by eq. (2), *i.e.*, $\mathbf{V}_{spin}^{(i), global}$.

Incorporation of temperature effects. – At $T > 0$, a cluster, when thermalized in a heat bath, is described by the canonical probability distribution function of total energy, $P_T(E)$, which specifies the probability that the system will be found in the energy interval $[E, E + \Delta E]$ at the specified temperature T . The distribution function corresponding to this temperature, within the canonical ensemble description, is (see refs. [14, 15] and references therein):

$$P_T(E) = \frac{n_T(E)}{N_T} = \frac{[\Delta\Gamma(E)] e^{-E/k_B T}}{Z_T}, \quad (4)$$

where $n_T(E)$ is the number of states in the energy interval $[E, E + \Delta E]$, N_T is the total number of accessible states, k_B is Boltzmann's constant, $\Delta\Gamma(E)$ the number of all the different states with energy in the interval $[E, E + \Delta E]$, $Z_T = \sum_i \exp[-\beta E_i] = \sum_{E_i} \Delta\Gamma(E_i) \exp[-\beta E_i]$ the partition function at temperature T and $\beta = 1/(k_B T)$.

To obtain $n_T(E)$ we proceed with the further generalization of our TBMD scheme for the $T = 0$ case [10]. This is achieved by incorporating the Nose-Hoover thermostat method [16–18] which is a constant-temperature method in an extended-system scheme that includes an extra degree of freedom which ensures that the system is in thermodynamic equilibrium with a heat bath [19].

A molecular-dynamics (MD) simulation at a given temperature T_j , $j = 1, 2, \dots, M$, ($M \approx 100$) provides numerical values for $n_{T_j}(E_i)$ at a discrete set of accessible equidistant energy values E_i , $i = 1, 2, \dots, N$, ($N = 10000$). Having obtained these, we make use of the proposed Multiple Histogram Method (MHM) [20], and obtain the values of $\Delta\Gamma(E)$ from which it is easy to obtain a smooth curve for the partition functions Z_{T_j} , $j = 1, \dots, M$. From these we can obtain any other thermodynamic quantity related to the partition function. It is recalled that the microcanonical entropy can be obtained from the equation $S(E) = k_B \ln[\Delta\Gamma(E)]$ (within an additive constant).

It should be understood, however, that a limiting factor in our method is the efficiency of the MD in sampling partition functions. We address this by taking special care to minimize problems associated with its use. This was achieved as follows:

- Wherever available, we started our simulations with cluster geometries corresponding to global minimum in the Sutton-Chen potential description, using the Cambridge cluster data base [21]. In cases when this was not available, we attempted to reach global optimization with our computer codes.
- We used a very large number of MD time steps (10000000 steps corresponding to 0.1 ns simulation time) and made sure that no abrupt changes occurred to states of lower energy while the thermodynamic equilibrium was reached seamlessly during the final and largest part of the simulation time even at elevated temperatures.
- We double-checked our MHM results by averaging directly over the time steps.

Computational details. – In order to make our computations feasible we first reach the thermodynamic equilibrium at each temperature using a classical interatomic potential which gives results as close as possible to our TB ones. While reaching the thermodynamic equilibrium, we apply our TB formalism (as generalized in the present work) every 100 time steps in order to calculate the MM of the cluster. In the MM calculation the cluster geometry is assumed frozen (as obtained using the classical potential approach at that particular time step) and the calculation of the MM of the cluster is repeated for a large number, $N_{ran}^{(i)}$, of atomic *spin configurations* taken randomly over the i -th *structural configuration* ($N_{ran}^{(i)} \approx 120$ –300 in the present calculations for every i -time step as dictated by our convergence criteria; *i.e.*, convergence as N_{ran} is increased). In view of these results, the average magnetic moment, $\bar{\mu}_{cl}^{(i)}$, per cluster atom during the i -th time step is defined as follows:

$$\bar{\mu}_{cl}^{(i)} = \frac{1}{N_{cl}} \left| \sum_k^{N_{cl}} \sum_j^{N_{ran}^{(i)}} \boldsymbol{\mu}_k^{j,i} e^{-(E_i^j - E_0^{(i)})/k_B T} \right|, \quad (5)$$

where $\boldsymbol{\mu}_k^{j,i}$ is the magnetic moment of the k -th cluster atom at the j -th magnetic configuration of the i -th time step. In case we want to calculate the projection $\bar{\mu}_{cl,\zeta}^{(i)}$ of $\bar{\mu}_{cl}^{(i)}$ on a specific ζ -direction (*i.e.*, that of an external magnetic field) we can just replace $\boldsymbol{\mu}_k^{j,i}$ by $\mu_k^{j,i} \cos \gamma_k^{j,i}$ in eq. (5), where $\gamma_k^{j,i}$ is the angle between the specified direction and the direction of the magnetic moment $\boldsymbol{\mu}_k^{j,i}$. In eq. (5), N_{cl} denotes the number of cluster-atoms and it has been assumed that each j -spin configuration contributes to the magnetic state of the i -th geometric configuration with probability $P_M(E_i^j) = e^{-(E_i^j - E_0^{(i)})/k_B T}$ and that $\sum_j^{N_{ran}^{(i)}} e^{-(E_i^j - E_0^{(i)})/k_B T} = 1$. The last equation is satisfied by normalizing the probabilities, *i.e.*, by deviding all probabilities by their sum. The index j denotes quantities evaluated at the particular j -th random atomic spin configuration of the i -th structural configuration of the cluster. $E_0^{(i)}$ is taken to be the energy of the ferromagnetically aligned atomic-spin configuration at the i -th time step; it is incorporated for numerical reasons, *i.e.*, in order to avoid underflows or overflows. In this way we take the average over the low-lying spin configurations of the cluster of a particular (frozen) geometric structure (*i.e.*, as calculated at the specific time step). Finally, the thermodynamic average of $\bar{\mu}_{cl}^{(i)}$ given by eq. (5) over the various cluster geometric structures (*i.e.*, time steps) is obtained by averaging over the time steps (over which we calculated the MM) or with the help of the probability $P_T(E)$ as given by eq. (4).

Results. – We next apply the present formalism to the Ni_n clusters of small and intermediate sizes. For the latter size, there exist relevant experimental results necessary for comparison. For Ni, the classical Sutton-Chen potential [22] is used as this was found to give results closer in agreement with our TBMD method than any other among the existing classical potentials for Ni [23,24]. The TBMD-parameters used in the present work were taken from ref. [13]. Results for two cluster sizes are presented, namely for Ni_{43} and Ni_{201} . In fig. 1 we present the Lindemann index and the specific heat per atom for both Ni_{43} and Ni_{201} as obtained using the classical potential approximation. From this it can be seen that the transition from solid to liquid starts at the transition temperature $T_{tran}(\text{Ni}_{43}) \approx 370$ K and $T_{tran}(\text{Ni}_{201}) \approx 780$ K for Ni_{43} and Ni_{201} , respectively. The solid-to-liquid transition appears to take place over a wide range of temperatures for the Ni_{43} cluster indicating a series of structural phase transitions. Snapshots of the Ni_{43} equilibrium geometries near $T_{tran}(\text{Ni}_{43})$ are depicted in fig. 2. In these, the beginning of a bond breaking process and a transformation of the initial ZT fcc structure to a rather complicated one resembling a twinning geometry are apparent. For the Ni_{201} cluster,

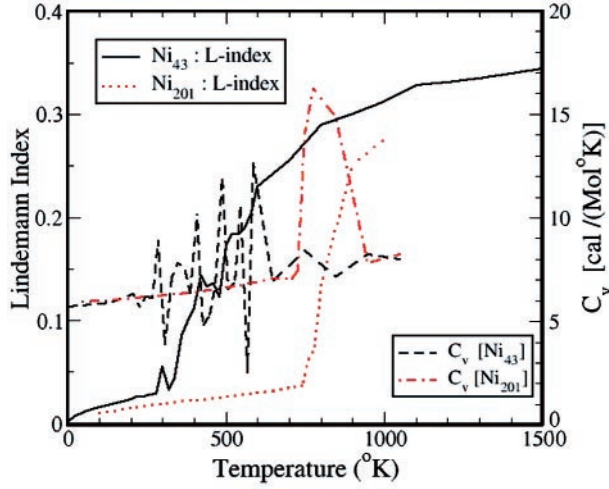


Fig. 1 – The Lindemann index and the specific heat for Ni_{43} and Ni_{201} clusters as obtained using the Sutton-Chen potential [22].

on the other hand, only one structural phase transition appears and, therefore, the transition range is much narrower. In fig. 3 we show the temperature dependence of the MM per atom, $\mu(T)$, of the Ni_{43} and Ni_{201} clusters as obtained using the TB-formalism presented in the above along with the existing experimental results for comparison. In particular, in fig. 3 experimental findings of Gerion *et al.* [6] for $\text{Ni}_{200-240}$ clusters and that of Apsel [25] are included. It is interesting to note that a decrease in the component of the total MM of the cluster along a particular direction is accompanied by a non-negligible decrease in the average value of the MM of the cluster atoms as a result of the structural changes with temperature. This is shown in fig. 3 where $\bar{\mu}_{cl}^{(i)}$ and $\bar{\mu}_{cl,z}^{(i)}$ are plotted for Ni_{43} . Following the procedure of Gerion *et al.* [6], we also calculated the temperature dependence of the magnetic contribution to the specific heat of the Ni_{43} and Ni_{201} clusters as obtained by taking the derivative $d\{\mu(T)\}^2/dT$ of the corresponding $\mu(T)$ curves. These results are also shown in fig. 3 along with the results of Gerion *et al.* Recalling that T_C^{cl} can be located by the maximum of the magnetic contribution to C_V (shown in fig. 3), it is found that $T_C^{cl}(\text{Ni}_{43}) = 310$ K and $T_C^{cl}(\text{Ni}_{201}) = 620$ K.

Our results for both Ni_{43} and Ni_{201} clusters indicate that $T_C^{cl} < T_{tran}$, *i.e.*, the Curie temperature for the cluster is smaller than the temperature which specifies the structural phase transition (the latter as derived from the classical potential approximation shown in fig. 1).

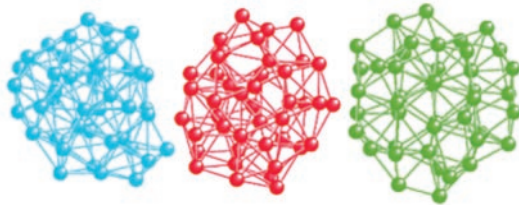


Fig. 2 – Snapshots of the equilibrium structures (*i.e.*, in thermodynamic equilibrium) of the Ni_{43} cluster at (left) 400 K, (middle) 500 K and, (right) 600 K.

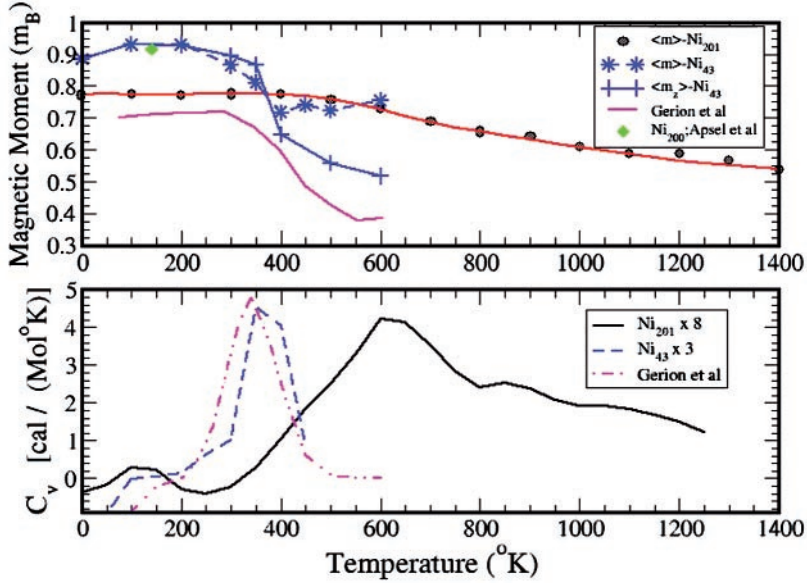


Fig. 3 – The calculated temperature dependence of the magnetic moment per atom (upper panel) and the specific heat (lower panel) of the Ni₄₃ and Ni₂₀₁ clusters as obtained in the present work along with reported experimental results.

This observation indicates that Ni_n begins to develop a strong paramagnetic character (*i.e.*, increase in the degree of disorder with respect to the orientations of the atomic magnetic moments) near but prior (and incoherently) to a structural phase transition. Compared to the results of Gerion *et al.* [6], our calculated T_C value for Ni₂₀₁ is somewhat larger than their experimentally found $T_C^{cl,exp}(\text{Ni}_{200-240}) = 340$ K and their theoretically calculated value ($T_C^{cl}(\text{Ni}_{200-240}) = 420$ K) within the mean-field theory [6]. However, our results are much closer to the estimated $T_C^{cl}(\text{Ni}) \approx 570$ K by Apsel *et al.* [25], and appear to have reached the bulk T_C value for Ni (625 K). Additionally, it is also worth noting that our results predict correctly an increase in the Curie temperature of a magnetic cluster as its size increases. From fig. 3 it is apparent that our results for Ni₄₃ rather than those for Ni₂₀₁ are in better agreement with the experimental results of Gerion *et al.* [6], the latter referring to clusters consisting of 200–240 atoms. This may be considered as accidental and not to be taken seriously as an issue for quantitative comparison between theory and experiment. This is because the existing experimental results are not only very limited but also in substantial disagreement among themselves. In particular, the results for the magnetic moments reported by Apsel *et al.* [25] differ by approximately 25% from those of Gerion *et al.* [6], while the difference in the corresponding values for T_C is much larger.

As seen in fig. 3, the data for Ni₄₃ exhibit a temperature range, namely between 300 and 370 K, where $\langle m_z \rangle$ is larger than $\langle m \rangle$. This is a consequence of the progressive establishment of non-collinearity of the atomic magnetic moments as the cluster reaches its structural transition temperature. As a result, and in accordance with the defining eq. (5) and the following discussion, $\langle m \rangle$ can become smaller than $\langle m_z \rangle$.

Finally, it is apparent from both the experimental results of Gerion *et al.* [6] and the present theoretical ones that $\mu(T)$ increases initially with T as was discussed in our previous

report [19]. However, the subsequent observed parabolic drop of MM with temperature does not go to zero at T_C^d . Instead, MM starts deviating from the parabolic behavior exhibiting a rather long tail. This may be interpreted as an indication that states with completely random orientation of the MMs of the cluster atoms are not energetically favorable for single-domain particles as is the case of the very small clusters.

In summary, we have introduced a unified approach that combines spin-orbit interactions with temperature effects for performing molecular-dynamics simulations of transition metal clusters. Application of the method to Ni clusters of small and intermediate sizes has produced results in good agreement with existing experimental results.

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REFERENCES

- [1] KNICKELBEIM M. B., *J. Chem. Phys.*, **116** (2002) 9703.
- [2] ODA T., PASQUARELLO A. and CAR R., *Phys. Rev. Lett.*, **80** (1998) 3622.
- [3] KATO M. and KOKUBO F., *Phys. Rev.*, **49** (1994) 8864.
- [4] OJEDA M. A., DORANTES-DAVILA J. and PASTOR G., *Phys. Rev. B*, **60** (1999) 6121.
- [5] STOCKS M. and WANG Y., report (1999) http://www.psc.edu/science/Wang/magnetic_moments.html.
- [6] GERION D., HIRT A., BILLAS I. M. L., CHATELAIN A. and DE HEER W. A., *Phys. Rev. B*, **62** (2000) 7491.
- [7] HOU M., AZZAOURI M. E., PATTYN H., VERHEYDEN J., KOOPS G. and ZHANG G., *Phys. Rev. B*, **62** (2000) 5117.
- [8] SCHMIDT M., KUSCHE R., HIPPLER T., DONGES J., KRONMULLER W., VON ISSENDORFF B. and HABERLAND H., *Phys. Rev. Lett.*, **86** (2001) 1191.
- [9] BANSMANN J. *et al.*, *Surf. Sci. Rep.*, **56** (2005) 189.
- [10] ANDRIOTIS A. N. and MENON M., *Phys. Rev. B*, **57** (1998) 10069.
- [11] UHL M., SANRDATSKII L. M. and KUBLER J., *Phys. Rev. B*, **50** (1994) 291.
- [12] ANDERSON P. W. and HASEGAWA H., *Phys. Rev.*, **100** (1955) 675.
- [13] ANDRIOTIS A. N. and MENON M., *Phys. Rev. Lett.*, **93** (2004) 026402.
- [14] SCHMIDT M., KUSCHE R., KRONMULLER W., VON ISSENDORFF B. and HABERLAND H., *Phys. Rev. Lett.*, **79** (1997) 99.
- [15] FANOURGAKIS G. S., FARANTOS S. C., PARNEIX P. and BRECHIGNAC PH., *J. Chem. Phys.*, **106** (1997) 4954.
- [16] NOSE S., *J. Chem. Phys.*, **81** (1984) 51.
- [17] HOOVER W. G., *Phys. Rev. A*, **31** (1985) 1965.
- [18] EVANS D. J. and HOLIAN B. L., *J. Chem. Phys.*, **83** (1985) 4069.
- [19] FTHENAKIS Z., ANDRIOTIS A. N. and MENON M., *J. Chem. Phys.*, **119** (2003) 10911.
- [20] WEERASINGHE S. and AMAR F. G., *J. Chem. Phys.*, **98** (1993) 4967.
- [21] DOYE J. P. K. and WALES D. J., *New. J. Chem.*, **22** (1998) 733.
- [22] SUTTON A. P. and CHEN J., *Philos. Mag. Lett.*, **61** (1990) 139.
- [23] FTHENAKIS Z., ANDRIOTIS A. N. and MENON M., in preparation.
- [24] ERKOS S., *Annual Reviews of Computational Physics IX*, edited by STAUFFER D., Vol. **IX** (World Scientific) 2001, p. 1.
- [25] APSEL S. E., EMMERT J. W., DENG J. and BLOOMFIELD L. A., *Phys. Rev. Lett.*, **76** (1996) 1441.