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The size effect in the equation of state for nanostructures

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Abstract
In analogy to the interacting real gas the magnetic systems are described like magnons which form the system of interacting quasi-particles. In order to describe the magnetic systems, firstly the equation of state for real gas is introduced and next the model is developed in the case of magnons for the confined geometry. In particular, the applications of magnetic equation of states for thin films and nanowires with unit cell cross sections as well as for nanoparticles are considered.

Moreover, the size effect and the critical temperature for the mentioned systems are investigated. The critical temperature and magnetization exhibit a strong dependence on the size of the system and the anisotropy of magnetic interaction in the interior and at the surface of the considered system.

1. Introduction

The development of microelectronics for devices with reduced dimensional scales constitutes a challenge for physicists working in nanotechnology. It is a frequent case in nanoelectronics that the length scales of the fundamental processes are comparable with the geometrical size of the device while the fundamental timescales are of the order of the time parameters of device operation comparable with the geometrical size of the samples.

From the theoretical point of view micromagnetic theory as well as first-principles computer calculations seem to be the best ways to describe phenomena in the nanoscale. Now they have reached a high level of sophistication and, moreover, they require relatively time-consuming calculations in comparison with the analytical treatment of problems. Generally, the above two methods are not able to bridge several orders of magnitude in multi-scale problems. The aim of the present paper is to develop the equation of state for the nanoscale magnetic objects as the confined systems. In order to describe their properties we take into account the analogy of the magnetic equation of state construction to the procedure applied in the case of the interacting real gas or the solid state crystalline nano-objects whose particles are considered as phonons. In this analogy the magnetic systems are described as magnons which form the system of interacting quasi-particles. For this purpose we introduce first the equation of state for a real gas, then we find the analogy to the phonons and finally we develop a model in the case of magnons.

In the context of nanoparticles the construction of the model requires consideration of the size effect which should be taken into account. We investigate the thin films, nanowires with unit cell cross sections and small nanoparticles for which the magnetization, its profile as well as the critical temperature of phase transition in their geometry dependence are discussed.

2. General formalism

An equation of state can be understood as a functional relation between the state variables for a system in equilibrium which reduces the number of independent degrees of freedom necessary to describe the behavior of the system.

For the aim of the present paper we consider the magnetic system as one of many particular examples. The considerations are based on the scheme introduced by Toop [1] for the PVT system (cf appendix). The thermodynamical variables for the magnetic systems are the intensity of the magnetic field h, the magnetization M and the temperate T. The analogous equations to (A.1) and (A.2) given in the appendix for the magnetic system can be obtained by the substitution $h \Leftrightarrow -P$, $M \Leftrightarrow V$ and then they can be rewritten in the form [2]

$$h = T\left(\frac{\partial h}{\partial T}\right)_M + \left(\frac{\partial U}{\partial M}\right)_T \qquad (1)$$

$$M = T\left(\frac{\partial M}{\partial T}\right)_h + \left(\frac{\partial H}{\partial h}\right)_T. \tag{2}$$

Multiplying (A.3) and (A.4) it is easy to obtain

$$\left[h - \left(\frac{\partial U}{\partial M}\right)_T\right]\left[M + \left(\frac{\partial H}{\partial h}\right)_T\right] = T^2\left(\frac{\partial h}{\partial T}\right)_M\left(\frac{\partial M}{\partial T}\right)_h. \tag{3}$$

Taking into account the relation [3]

$$T\left(\frac{\partial h}{\partial T}\right)_M\left(\frac{\partial M}{\partial T}\right)_h = -(C_h - C_M) \tag{4}$$

and substituting it in equation (3) we obtain

$$\left[\left(\frac{\partial U}{\partial M}\right)_T - h\right]\left[M + \left(\frac{\partial H}{\partial h}\right)_T\right] = T(C_h - C_M) \tag{5}$$

where C_h and C_M represent the heat capacity at constant field and constant magnetization, respectively.

The last equation is called the rigorous equation of state for magnetic materials. It was obtained by Balcerzak [4] in analogy to the equation of state for solids, liquids and gases discussed by Toop [1].

An alternative form of (5) can be proposed by taking into account the relation

$$\mathrm{d}Q = T\,\mathrm{d}S = T\left(\frac{\partial S}{\partial T}\right)_h \mathrm{d}T + T\left(\frac{\partial S}{\partial h}\right)_T \mathrm{d}h. \tag{6}$$

For reversible process we can also write

$$\mathrm{d}Q = T\,\mathrm{d}S = T\left(\frac{\partial S}{\partial T}\right)_M \mathrm{d}T + T\left(\frac{\partial S}{\partial M}\right)_T \mathrm{d}N. \tag{7}$$

(A.6) can be rewritten in the form

$$\mathrm{d}Q = T\,\mathrm{d}S = \left[T\left(\frac{\partial S}{\partial T}\right)_M + T\left(\frac{\partial S}{\partial M}\right)_T\left(\frac{\partial M}{\partial T}\right)_h\right]\mathrm{d}T + T\left(\frac{\partial S}{\partial M}\right)_T\left(\frac{\partial M}{\partial h}\right)_T \mathrm{d}h. \tag{8}$$

Comparing (8) with (6) we find

$$C_h = T\left(\frac{\partial S}{\partial T}\right)_h = C_M + T\left(\frac{\partial S}{\partial M}\right)_T\left(\frac{\partial M}{\partial T}\right)_h. \tag{9}$$

Substituting (9) in equation of state (5) we obtain an alternative form of (5):

$$\left[\left(\frac{\partial U}{\partial M}\right)_T - h\right]\left[M + \left(\frac{\partial H}{\partial h}\right)_T\right] = T^2\left(\frac{\partial S}{\partial M}\right)_T\left(\frac{\partial M}{\partial T}\right)_h. \tag{10}$$

This form of the equation of state for the magnetic system seems to be important from the point of view of applications, for example, for the description of the magnetocaloric effect (MCE) in magnetic systems as well as of the giant magnetoresistance in nanoparticles. On the right-hand side of (10) the derivative of magnetization and entropy appears with respect to temperature and magnetization, respectively.

As an illustrative example of the present considerations we would like to show the form of the equation of state for a very simple case, i.e. for the molecular field approximation. For the Hamiltonian

$$H = -\tfrac{1}{2}\sum_{i,j}^{N} J_{ij}S_iS_j - h\sum_{i=1}^{N} S_i \tag{11}$$

where $S_i = \pm 1$, S_i is the z component of the spin while N is the number of spins in the system. In the molecular field approximation (MFA)

$$\langle S_iS_j\rangle \approx \langle S_i\rangle\langle S_j\rangle = m^2. \tag{12}$$

We assume that $M = \langle\sum_i S_i\rangle = N\langle S_i\rangle = Nm$. The internal energy U is given by the relation

$$U = -\frac{1}{2}J\sum_{i,j} S_iS_j = -\frac{NzJm^2}{2} \tag{13}$$

while the Gibbs–Boltzmann (BG) entropy is of the form

$$S = -\frac{k_\mathrm{B}N}{2}[(1+m)\ln(1+m) + (1-m)\ln(1-m)] = \frac{k_\mathrm{B}}{2}\left[(N+M)\ln\left(\frac{N+M}{N}\right) + (N-M)\ln\left(\frac{N-M}{N}\right)\right] \tag{14}$$

where the enthalpy is $\langle H\rangle = \frac{1}{2}NzJm^2 + NhM$.

Taking into account the relations (13) and (14) we substitute them into (10) and obtain

$$\left(h + \frac{zJM}{N}\right)^2\left(\frac{\partial M}{\partial h}\right) = T^2\left(\frac{\partial S}{\partial M}\right)_T\left(\frac{\partial M}{\partial T}\right)_h = -\frac{k_\mathrm{B}T^2}{2}\ln\left(\frac{N+M}{N-M}\right)\left(\frac{\partial M}{\partial T}\right)_h. \tag{15}$$

The last equation is equivalent to the following set of equations:

$$\left(h + \frac{zJM}{N}\right) = \frac{k_\mathrm{B}T}{2}\ln\frac{N+M}{N-M} \tag{16}$$

$$\left(h + \frac{zJM}{N}\right)\left(\frac{\partial M}{\partial h}\right)_T = -T\left(\frac{\partial M}{\partial T}\right)_h. \tag{17}$$

Solving equation (16) with respect to M we obtain the well-known formula for magnetization:

$$M(h,T) = Nth\left(\frac{JzM + hN}{Nk_\mathrm{B}T}\right) = Nth\left(\frac{Jzm + h}{k_\mathrm{B}T}\right) \tag{18}$$

while equation (17) constitutes the identity which is easy to verify using the relation (18). For this case we consider here the equation of state which can be simplified to the equation

$$\left[\left(\frac{\partial U}{\partial M}\right)_T - h\right] = T\left(\frac{\partial S}{\partial M}\right)_T. \tag{19}$$

3. Equation of state for the reduced dimension system

The equation of state introduced above in the form of (10) or equivalently by (5) is general and can be satisfied for the finite homogeneous system which is characterized by the internal energy, enthalpy, entropy and the order parameter, i.e. magnetization. But the question arrives: how to extend the equation of state for the inhomogeneous systems such as the small (nano-) systems characterized by a size of the order of the correlation length [5] and for the finite case with the reduced dimension (thin films, multilayers, wires of unit cell cross section, small nanoparticles)?

To find the answer to the last questions we take into account the analogy between the considerations presented by Hill [6] for thin solid films and the approach applied for the inhomogeneous system due to thermodynamic fluctuations [7]. The inhomogeneity in this case is connected with the geometrical structure, i.e. the breaking of the translational symmetry in the direction perpendicular to the surface.

The inhomogeneities can be treated as the deviation of the thermodynamical quantity from its mean value determined for the whole system considered as homogeneous. In order to evaluate the mean value of the global characteristics we divide the whole inhomogeneous system into identical subsystems which are assumed to be homogeneous.

The description of the system is achieved by the averaging procedure used for static fluctuations. The total energy is the sum of the energies of subsystems which are considered to be homogeneous. In practice it means the averaging of the equation of state. In the case of the equation of state for the gas we have

$$\left\langle \left[p+\left(\frac{\partial U}{\partial V}\right)_T\right]\left[V-\left(\frac{\partial H}{\partial P}\right)_T\right]\right\rangle = \langle T(C_p - C_V)\rangle. \qquad (20)$$

Because p, V and T are the global variables the averaging of (20) leads to the equation of state for the inhomogeneous system:

$$\left[p+\left\langle\left(\frac{\partial U}{\partial V}\right)_T\right\rangle\right]\left[V-\left\langle\left(\frac{\partial H}{\partial P}\right)_T\right\rangle\right]+\Delta$$
$$= T\langle(C_p - C_V)\rangle \qquad (21)$$

$$\Delta = \left\langle\left(\frac{\partial U}{\partial V}\right)_T\right\rangle\left\langle\left(\frac{\partial H}{\partial V}\right)_T\right\rangle - \left\langle\left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial H}{\partial V}\right)_T\right\rangle \qquad (22)$$

where the term Δ given by (22) represents the thermodynamic correlation for the inhomogeneous system and is a measure of the inhomogeneity of the system. Of course $\Delta = 0$ when the system becomes homogeneous. In analogy to the equation of state for a gas described by variables P, V and T the equation of state for the magnetic system can also be introduced. However, we should remember about the limitation that we consider a small system in the nanoscale. These limitations are related to the fact that all thermodynamics is based on the assumption that the number of particles or atoms N and volume V are very large ($N, V \rightarrow \infty$) and the system is translationally invariant. In the mathematical language in the thermodynamical limit we should use intensive quantities, i.e. independent of the size of the system. The thermodynamical function used for the description of the system should include the limitations of the finite size of the system.

In the context of the considerations introduced by Hill [6] the average value $\langle x\rangle$ of the thermodynamic quantity x for the inhomogeneous system for a thin solid film with thickness d can be expressed [8] by (21):

$$\langle x\rangle = \langle x\rangle_0 + \frac{1}{d}\langle x\rangle_1 \qquad \langle x_0\rangle = \langle x\rangle_{3D}$$
$$\langle x\rangle_1 = \langle x\rangle_{2\mathrm{D}} - \langle x\rangle_{3\mathrm{D}} \qquad (23)$$

where $\langle x\rangle_0$ denotes the mean value of x when the system is homogeneous while $\langle x\rangle_1$ represents the difference between the two-dimensional and three-dimensional average value of x. The last formula includes the size effect in the context of hierarchical equations of state proposed by Hill [6].

If we consider the phonons propagating in the restricted dimension, for example the thin films of thickness d, the values of $(\frac{\partial U}{\partial V})_0$, $(\frac{\partial U}{\partial V})_1$, $(\frac{\partial H}{\partial p})_0$, $(\frac{\partial H}{\partial p})_1$ can be evaluated by means of the caloric equation of state for the internal energy U and enthalpy which, in the case of the pseudoharmonic approximation [9], leads to the result

$$\left(\frac{\partial U}{\partial V}\right)_1 = -2z_1 a\left(\frac{\partial U}{\partial V}\right)_0 \qquad (24)$$

where z_1 stands for the number of nearest neighbors missing for the surface atoms while a is the lattice constant. If we suppose that the volume of the considered system is fixed, i.e. $(\frac{\partial H}{\partial p})_0 = V_0$ and $(\frac{\partial H}{\partial p})_1 = 0$. Equation (21) for $\Delta = 0$ can be rewritten in the form of (20) by means of the reduced variables

$$\bar{p} = p\frac{1}{1-\frac{2z_1 a}{d}} \qquad (25)$$

and

$$\bar{T} = T\frac{1}{1-\frac{2z_1 a}{d}}. \qquad (26)$$

The thermal and pressure renormalization is connected with the lattice vibrations. The renormalization procedure can be given by the decoupling of the Green functions applied to the calculations of the thermodynamic averages for the considered system [10]. The renormalized effective potential describing the interaction between two atoms embedded in a system of atoms can be expanded in a series of powers of the reduced relative mean square displacement of neighboring atoms from their equilibrium position due to the lattice vibrations [11].

Next we limit our considerations to the system with restricted dimensions such as 0D structure-cube, 1D chain of the finite length and spherical nanoparticle and thin films. In a later part of this paper, we will consider only the confined magnetic systems.

3.1. 0D structure

We start our considerations for the structure of a cube given in figure 1. The exchange integral is independent of the

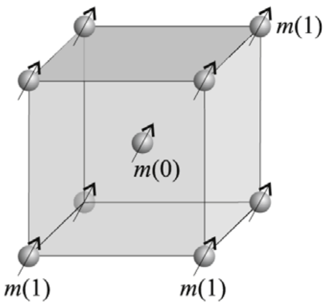

Figure 1. A single cube as an example of 0D structure.

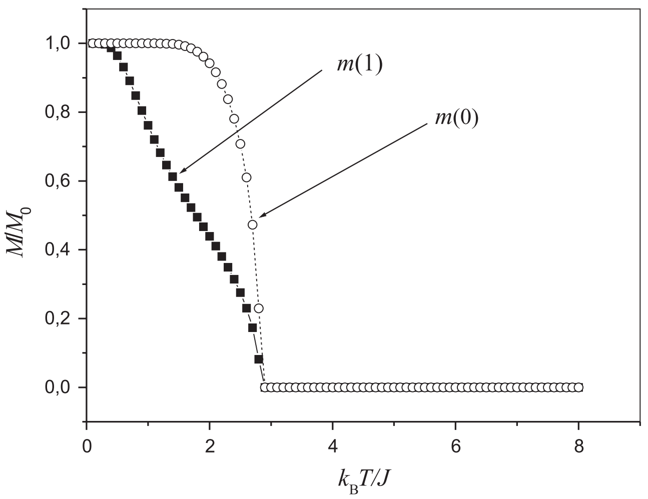

Figure 2. Magnetization of $0D$ structure as a function of reduced temperature T in k_{B}/J units.

crystallographic orientation. Within the MFA this fact leads directly to the following set of equations for magnetization of the considered system:

$$\begin{aligned} m(0) &= \tanh\left(\frac{Jm(1)z+h}{k_{\mathrm{B}}T}\right) \\ m(1) &= \tanh\left(\frac{Jm(0)z+h}{k_{\mathrm{B}}T}\right). \end{aligned} \qquad (27)$$

Equation (27) can be solved numerically and the results of calculations are given in figure 2.

The inhomogeneity of magnetization for the cube is well seen in spite of the fact that we suppose the isotropic interaction between the magnetic moment at the lattice side. Next, we try to estimate the Curie temperature for such a system. For temperatures close to the Curie temperature we can expand the tangent hyperbolic into a series and, as a consequence, the solubility conditions for the set of homogeneous equations given by (27) leads to

$$\begin{vmatrix} 1 & -\frac{Jz}{k_{\mathrm{B}}T} \\ -\frac{Jz}{k_{\mathrm{B}}T} & 1 \end{vmatrix} = 0. \qquad (28)$$

The solution of (28) determines the critical temperature given by $\frac{k_{\mathrm{B}}T_{\mathrm{C}}}{Jz} = 1$.

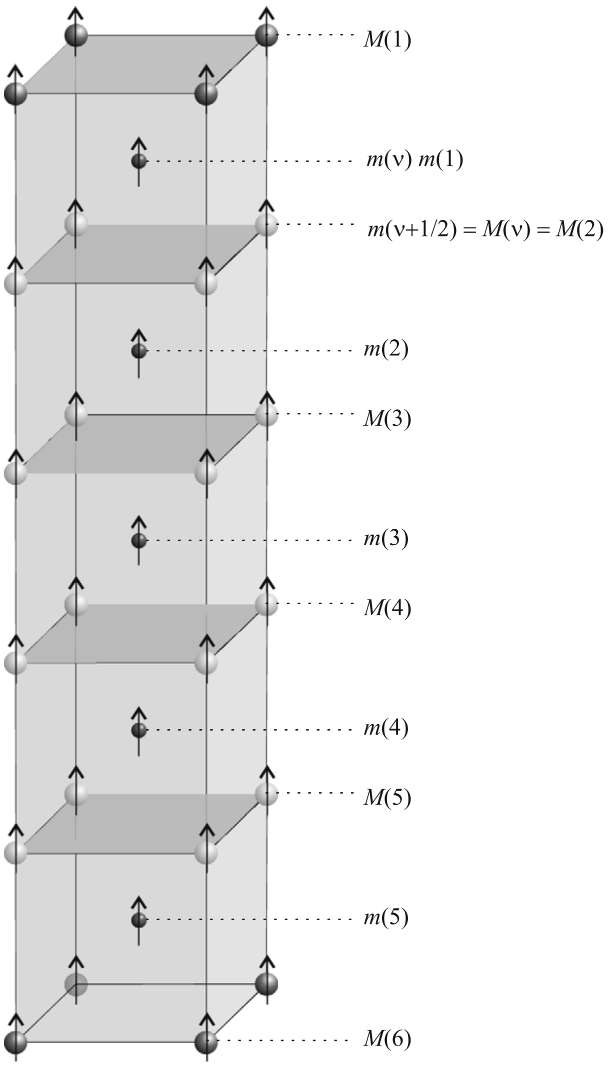

Figure 3. Structure of chain with the rectangular cross section in atomic scale.

3.2. Nanowire

Next, we consider the structure of wires (figure 3) including the finite number n of elementary cubes presented previously. As an illustrative example we show the calculations of magnetization and the critical temperature for $n = 3$. In analogy to our earlier considerations, and using the notation presented in figure 3, the magnetization for such a system is given by the solution of the following set of equations:

$$\begin{aligned} M(1) &= \tanh\left(\frac{Jm(1)}{k_{\mathrm{B}}T}\right) \\ m(1) &= \tanh\left(\frac{4J(M(1)+M(2))}{k_{\mathrm{B}}T}\right) \\ M(2) &= \tanh\left(\frac{J(m(1)+m(2))}{k_{\mathrm{B}}T}\right) \\ m(2) &= \tanh\left(\frac{4J(M(2)+M(3))}{k_{\mathrm{B}}T}\right) \\ M(3) &= \tanh\left(\frac{J(m(2)+m(3))}{k_{\mathrm{B}}T}\right) \end{aligned}$$

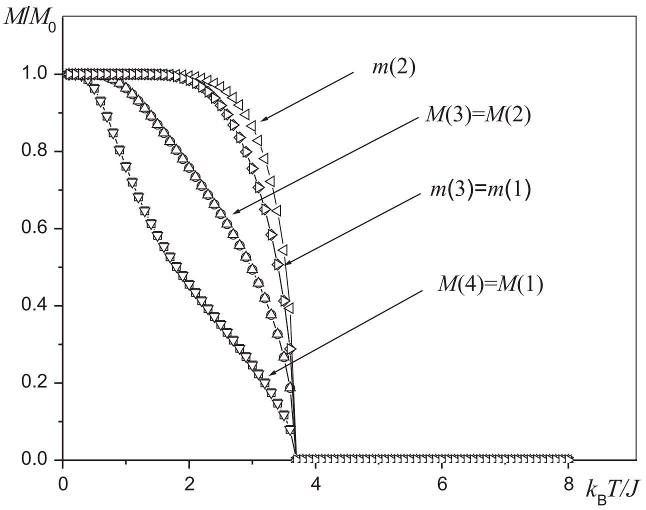

Figure 4. The inhomogeneity of magnetization for the rectangular cross-section atomic wires including three unit cells.

$$m(3) = \tanh\left(\frac{4J(M(3)+M(4))}{k_B T}\right)$$
$$M(4) = \tanh\left(\frac{Jm(3)}{k_B T}\right) \tag{29}$$

The magnetization is found by numerically solving a set of equations (29) and the results of calculations are given in figure 4. We observe that the magnetization of the outer planes (surfaces) $M(4) = M(1)$ is smaller than in the interior of the cubic chain. In figure 5 we plot the spatial evolution of the magnetic moment along the cubic wire at different temperatures. In the considered case the wire is $n = 25a$ long (a is the lattice constant). At all temperatures magnetization exhibits an oscillatory behavior; with an increase of the temperature the amplitude of magnetization oscillations is attenuated. Moreover, the magnetic moment at two outer surfaces is also lower that in the interior of the wire. The last fact can be easily reversed (magnetic moment at two outer surfaces can also be higher than the magnetic moment in the interior of the wire) by the assumption of the exchange constant at the surface region being different than in the bulk material or by introducing a different magnetic moment at the surface [12]. The critical temperature T_C for the considered case is found by solving the following equation:

$$\begin{vmatrix} 1 & \frac{-Jz}{k_BT} & 0 & 0 & 0 & 0 & 0 \\ \frac{-4J}{k_BT} & 1 & \frac{-4J}{k_BT} & 0 & 0 & 0 & 0 \\ 0 & \frac{-4J}{k_BT} & 1 & \frac{-4J}{k_BT} & 0 & 0 & 0 \\ 0 & 0 & \frac{-4J}{k_BT} & 1 & \frac{-4J}{k_BT} & 0 & 0 \\ 0 & 0 & 0 & \frac{-4J}{k_BT} & 1 & \frac{-4J}{k_BT} & 0 \\ 0 & 0 & 0 & 0 & \frac{-4J}{k_BT} & 1 & \frac{-4J}{k_BT} \\ 0 & 0 & 0 & 0 & 0 & \frac{-4J}{k_BT} & 1 \end{vmatrix} = 0. \tag{30}$$

Figure 6 shows an influence of the size effect (length of wire) on the critical temperature T_C. We observe the saturation of critical temperature for the chain of length larger than $n = 12$.

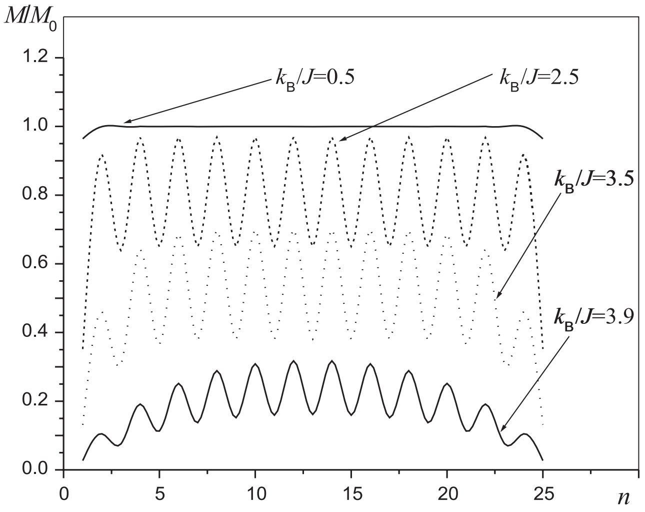

Figure 5. The inhomogeneity of magnetization for the rectangular cross-section atomic chain versus the number of unit cells in the chain for various reduced temperatures T in k_B/J units.

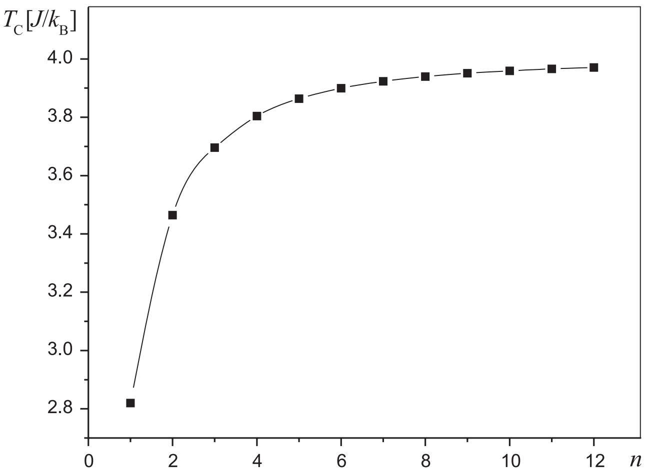

Figure 6. The critical temperature for the atomic chain of unit cells versus the length as an example of the confined system. We consider only the case when $J_s = J_b$.

3.3. Thin film

The thin layer is usually treated as a set of monoatomic layers parallel to the surfaces. In this case the total thickness of a film is $d = na$ where n is the number of monoatomic layers while a is the distance between two successive layers.

Each atom situated at the lattice side in the infinite plane (2D system) is surrounded by its z_0 nearest neighbors while the same atom embedded in a 3D structure has $z = z_0 + 2z_1$ neighboring atoms.

As a consequence, the difference of the internal energy derivative with respect to magnetization m for 3D system and 2D systems is equal to

$$\left(\frac{\partial U}{\partial m}\right)_{2D} - \left(\frac{\partial U}{\partial m}\right)_{3D} = -2z_1 Jm \tag{31}$$

and it has a negative sign, for example, in the case of the sc(100) lattice $z_0 = 4$ and $z_1 = 1$. Breaking translational symmetry in the direction perpendicular to the surface leads to the inhomogeneity of the magnetic order parameter for thin films. In particular, we consider the magnetic system of the magnetic moments localized in the crystallographic lattice site. For the confined systems we assume that $\langle x\rangle = m$, which leads to the following expressions for $(\frac{\partial U}{\partial m})_T$ and $(\frac{\partial S}{\partial m})$:

$$\frac{\partial U}{\partial m} = -NzJm \to -NzJ\left(m + \frac{1}{n}m_1\right) \tag{32}$$

$$\frac{\partial S}{\partial m} = -\frac{k_B T}{2}\ln\left(\frac{1+m}{1-m}\right) \to -\frac{k_B T}{2}\left[n\left(\frac{1+m+\frac{1}{n}m_1}{1-m-\frac{1}{n}m_1}\right)\right] \tag{33}$$

where m_1 denotes the difference of magnetization between the two-dimensional and three-dimensional structures.

Taking into account the relations (32) and (33) and substituting them in (19) we obtain the equation of state which can be easily transformed to the form

$$\left[\left(\frac{\partial U}{\partial M}\right)_T - \tilde{h}\right] = \tilde{T}\left(\frac{\partial S}{\partial M}\right)_T \tag{34}$$

in terms of reduced variables

$$\tilde{h} = \frac{h}{\left(1+\frac{1}{n}\frac{\langle x\rangle_1}{\langle x\rangle_0}\right)\left(1+\frac{1}{n}\frac{\langle y\rangle_1}{\langle y\rangle_0}\right)} \tag{35}$$

$$\tilde{T} = \frac{T}{\left(1+\frac{1}{n}\frac{\langle x\rangle_1}{\langle x\rangle_0}\right)\left(1+\frac{1}{n}\frac{\langle y\rangle_1}{\langle y\rangle_0}\right)} \tag{36}$$

where (34) for thin films is of the same form as (19) for the massive (bulk) material but it is written in terms of reduced variables $\tilde{h}, \tilde{T}$ which depend on the size of the sample. It means that the equation of state includes the size effect which is at the same time predicted for the phase transition temperatures and the instability points.

The critical temperature [13] can be determined from the equation

$$Jz = k_B\tilde{T}_C = \frac{k_B T_C(n)}{\left(1+\frac{1}{n}\frac{m_1}{m_0}\right)} \times\left\{1+\ln\left[\frac{1+m_0\left(1+\frac{1}{n}\frac{m_1}{m_0}\right)(1-m_0)}{(1+m_0)\left(1+m_0\left(1+\frac{1}{n}\frac{m_1}{m_0}\right)\right)}\right]\right\}^{-1} \tag{37}$$

and leads to the following relation:

$$\frac{T_C(n)}{T_C(\infty)} = \left(1+\frac{1}{n}\frac{m_1}{m_0}\right) \times\left\{1+\ln\left[\frac{1+m_0(1+\frac{1}{n}\frac{m_1}{m_0})(1-m_0)}{(1+m_0)(1+m_0(1+\frac{1}{n}\frac{m_1}{m_0}))}\right]\right\}. \tag{38}$$

The final formula for the critical temperature is given by

$$\frac{T_C(n)}{T_C(\infty)} = \left(1-\frac{2z_1}{z}\frac{1}{n}\right) \times\left\{1+\ln\left[\frac{1+m_0(1-\frac{2z_1}{z}\frac{1}{n})(1-m_0)}{(1+m_0)(1+m_0(1-\frac{2z_1}{z}\frac{1}{n}))}\right]\right\}. \tag{39}$$

Thus, the critical temperature for the considered system depends also on the size effect. Next, we consider the size effect in the case of a nanoparticle.

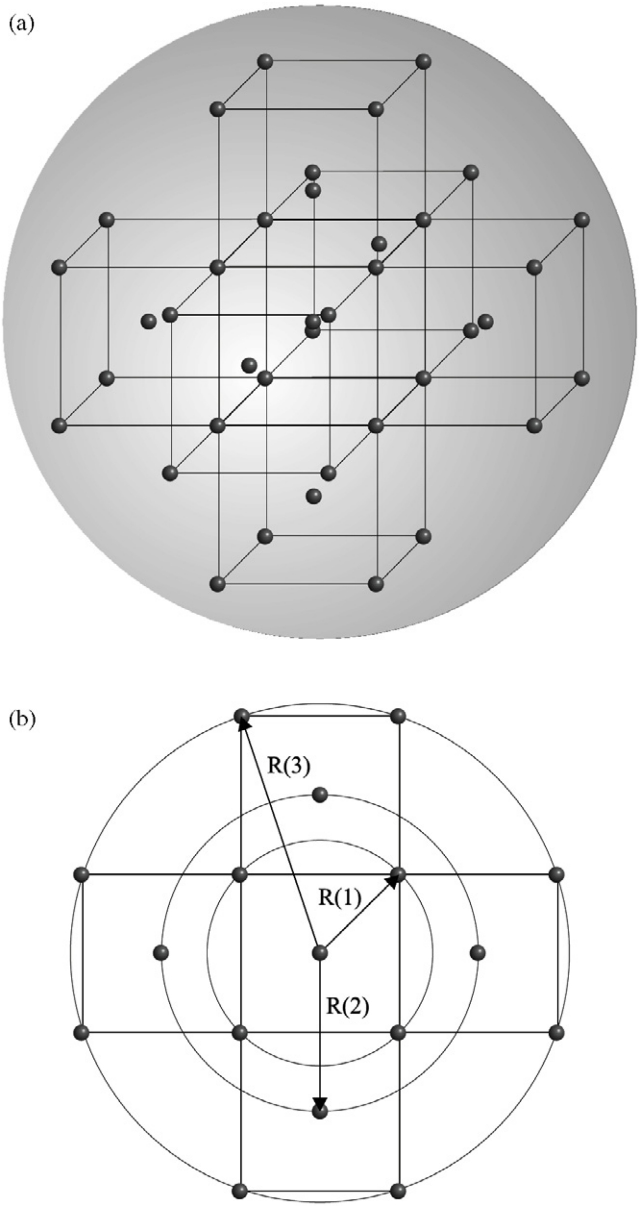

Figure 7. Schematic illustration of spherical particles. The quantization axes are oriented in one direction parallel to the z axis. (a) 3D plot of nanoparticle with bcc lattice type, (b) 2D cross section of nanoparticle, $R(1)$, $R(2)$ and $R(3)$ represent the radius of successive shells measured from the middle of nanoparticle.

3.4. Nanoparticle

A schematic illustration of nanoparticles is presented in figure 7. The breaking of translational symmetry in the direction perpendicular to the surface leads as a consequence to the fact that surface effects dominate the magnetic properties. Moreover, for the particles with diameters of the order of 8 nm 50% of atoms lie on the surface. This fact is much more pronounced still when the diameter of nanoparticles decreases. The magnetization near the surface can be lower [14, 15] or higher than in the interior [16] of a nanoparticle. The Mössbauer spectroscopy of maghemite performed for nanoparticles shows that the observed spectrum contains two components: one of them is associated with the

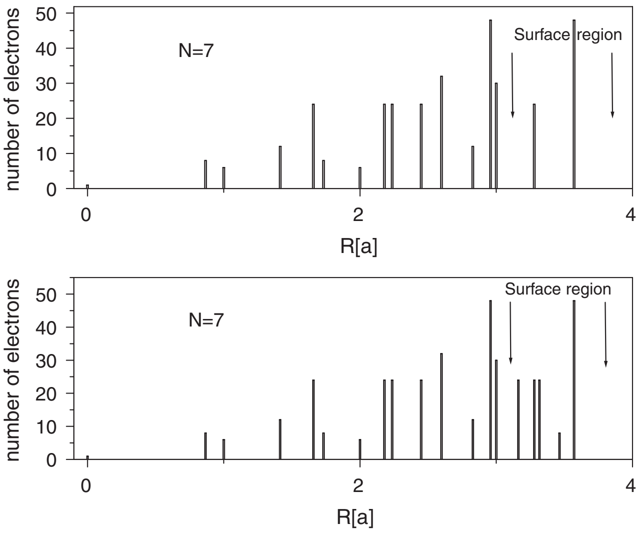

Figure 8. The number of electrons in shells as a function of distance in lattice constant units from the middle of a spherical particle. The upper panel shows the case when the sphere is filled only by whole cubes. The lower panel shows spherical particles occupying all lattice sites less than or equal to the radius R.

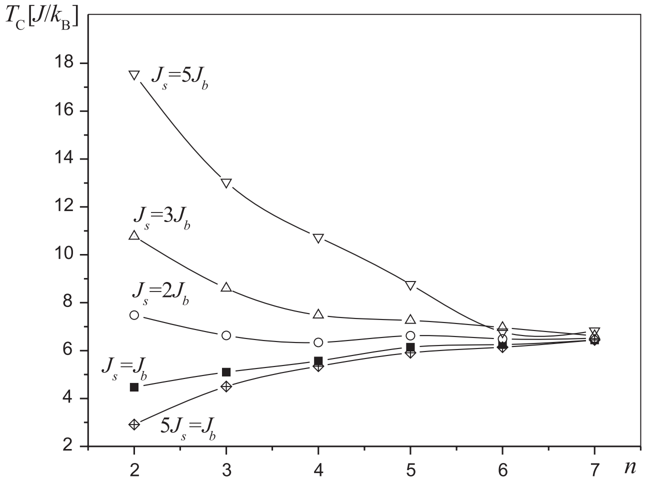

Figure 9. The critical temperature for spherical nanoparticles as a function of the number of shells.

atoms on the surface and the second in the interior [17]. The same effect was observed for the cobalt nanoparticles [18].

Recent experiments exhibited particle size scaling laws observed in the resonance peak frequency in the case of Fe–Ni nanoparticle [9]. The theoretical interpretation and analysis was made by Ferchmin and Puszkarski [20].

The magnetic fluctuation in the system of hematite nanoparticles has been investigated by means of inelastic neutron scattering [21]. The observed width of the inelastic peak increases with increasing temperature, which was correlated with the dynamics of spin waves in the particle for $q = 0$. Taking into account the last fact and using the spin wave model Mørup and Hansen [22] showed that the uniform precession mode which corresponds to a spin wave with wavevector $q = 0$ is predominant in nanoparticles.

The theoretical treatment of spin wave excitations was developed by Ferchmin and Puszkarski [23] using the matrix theory.

We start our considerations from spherical nanoparticles having a bcc crystallographic structure. First, we choose the middle of the nanoparticle and successive atoms occupying the lattice sides up to the diameter of the sphere. We suppose at the beginning that the sphere is packed (filled) only by whole cubes. In this case the nanoparticle is defined by the central spin located at the middle of the sphere and numbered as 1 and the other spins are situated on the shells around the middle of the particle and numbered $2, 3, \ldots, n$, where n denotes the total number of spherical shells and represents also the final shell of the surface of the nanoparticle. In figure 8 we present the distribution of spins on the successive shells for the nanoparticle of diameter $D = \sqrt{(7a)^2 + (\sqrt{2}a)^2} = \sqrt{51}a$ ($N = 7$), where N is the number of cubes which are packed into a distance equal to the diameter of the particle (D in this case represents a diagonal of a chain of $N = 7$ cubes), where a is the lattice constant for two cases. The first case (upper panel in figure 8) is when the sphere is packed by the whole elementary cells and the second (lower panel in figure 8) is when we suppose that all lattice sites are occupied. The distance is less than $D/2$ (when the sphere is packed by the partial elementary cells). In these two cases we have different packing coefficients (defined as a number of surface atoms to the total number of atoms in nanoparticle) at the surface. The difference is clearly seen because these additional shells constitute the surface region and, as a consequence, contribute to the surface effect. The label 'surface region' in figure 8 physically represents a few shells which constitute the external border of the sample. For further considerations we will discuss only nanoparticles of a spherical shape.

In figure 9 we show the influence of the size effect on the critical temperature of the spherical nanoparticle. The calculations are based on the formula (39) applied for the nanoparticle structure. It is observed that the critical temperature increases or decreases with an increase in the diameter of the particles and next tends to the saturation value; moreover, a strong dependence on the surface exchange constant is seen. The effect is strong for nanoparticles with a diameter less than $5a$ and depends also strongly on the value of the exchange constant at the surface J_s (the ratio J_s/J_b). The size effect is much more pronounced when the ratio J_s/J_b is larger (stronger magnetic interaction at the surface).

Figure 10 shows the profile of magnetization for a particle of diameter $D = 4.36a$ ($N = 7$) for the case when $J_s = J_b$. We observe that the magnetic moment at the surface is lower than in the middle of the particle. The oscillations across the radius of the nanoparticle are observed and the character of these oscillations as a function of reduced temperature is conserved. An analogous profile of magnetization for nanoparticles of diameter $D = 3.46a$ is shown in figure 11. The oscillations across the radius of the nanoparticle are attenuated with an increase in reduced temperature and the magnetic moment at the surface is lower than in the middle of the particle. In figure 12 we show the inhomogeneity of magnetization for the nanoparticle of diameter $D = 3.46a$ for

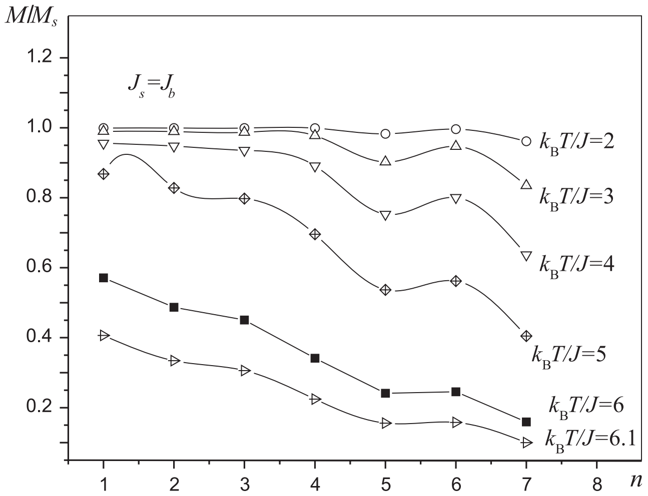

Figure 10. The inhomogeneity of magnetization for the spherical particle including seven shells $J_s = J_b$.

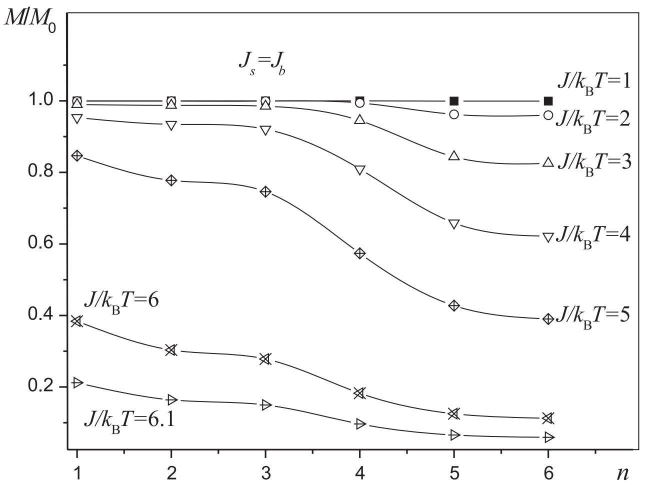

Figure 11. The profile of magnetization across the radius of particle ($D = 3.46a$) for different values k_BT/J and $J_s = J_b$.

$J_s = 5J_b$. The oscillatory character is conserved but the strong anisotropy of the magnetic interaction leads to higher magnetic moment at the surface in comparison with the magnetic moment in the interior of a particle. Finally, figure 12 shows and confirms the importance of the surface (here understood as the outer shell constituting the surface). In both the cases presented the magnetic moment at the surface is slightly higher than in the middle of the particle and less than in the interior of the particle. The significant importance of the surface finds experimental confirmation in the Mössbauer spectra of γ–Fe_2O_3 where the spectrum contains two components: one associated with the interior (bulk) of the particle and the second one with the atoms on the surface. The thickness of the surface region was estimated from the experiment as a layer of range thickness of 0.35 nm [24]. The effect of surface and finite size was considered also in [25], where the authors studied the thermal and spatial dependence of the magnetization of small nanoparticles on the simple cubic structure using the Monte Carlo technique. The state of the surface and the finite size effect were also considered in [26] in the context of their influence on the spin excitation spectrum.

By comparing figure 11 with 12 we can observe the oscillations of magnetization in the surface region versus temperature in the bcc structure. We should remember that if the number of surface atoms (spins) is larger the surface effect is much more pronounced. In all calculations and results presented earlier we suppose that in the majority of cases the interactions between the spins have an isotropic character. The assumption that the exchange constant has anisotropic nature, i.e. the surface atom interacts with another spin with exchange constant J_s while in the bulk it interacts with the coupling constant J_b, leads as a consequence to a different profile of magnetization close to the surface region. When $J_s < J_b$ it is possible to obtain the magnetization value which reduces close to the surface. In this case the observed magnetization oscillations are weaker.

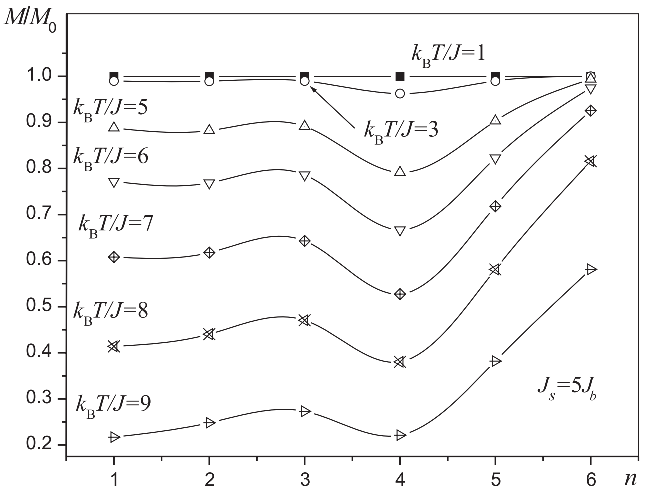

Figure 12. The profile of magnetization across the radius of particle ($D = 3.46a$) for different values k_BT/J and $J_s = 5J_b$.

4. Conclusions

The equation of state for magnetic systems was introduced in the context of the confinement of small systems in the nanoscale.

We considered the systems with confined dimensions such as 0D structure-cube, 1D wires represented by the chain of cubes with finite length, thin films and small nanoparticles.

Figures 4 and 5 show the inhomogeneity of magnetization for atomic rectangular cross-section wires and confirm the different behavior of the core and the surface contribution. The experimental investigations of the finite size effect in ZnO nanowires [31] show the enhancement of conductivity. This fact can be explained by the increase of the carrier concentration contributed by the enriched surface states and confirms that the surface plays a dominant role in the electrical and optical properties of the quasi-one-dimensional materials.

The typical behavior of critical temperature described by formula (39) was observed experimentally in thin films of Ni [34, 35] for different surface orientations.

The present paper brings several characteristics of nanoparticles obtained due to the size effect which appears in the system with restricted dimensions. Some of them are considered by other authors in their papers. First of all we would like to compare our results with the calculations presented by Mørup and Hansen [19] where the authors used the spin wave model to calculate the temperature dependence on the magnetization for a magnetic nanoparticle. The uniform precession mode is predominant in the nanoparticle and it gives rise to an approximately linear temperature dependence on magnetization in the low temperature limit. In the paper of Levy *et al* [27] the spin wave excitations were considered in the case of Co dots. The results show that in $2D$ systems the magnetization is determined by the value of the edge and bulk anisotropy. In the paper by Ferchmin and Puszkarski [20] the theoretical interpretation and analysis show in the case of Fe–Ni nanoparticles [28] that experiments exhibited particle size scaling laws observed in the resonance peak frequency.

The results which are particularly interesting refer to the behavior of the size effect for the Curie temperature shown in figure 10. We can see that the critical temperature increases or decreases with an increase of the diameter of particles and next tends to the saturation value; moreover, a strong dependence on the surface anisotropy is observed. The effect is stronger for nanoparticles with diameters less than $5.2a$ and depends also on the ratio of the exchange constant J_s/J_b. The size effect is much more pronounced when the ratio J_s/J_b is larger (larger anisotropy of magnetic interaction at the surface). The curves in figure 10 can be compared with the paper of Wesselinova and Apostolova where the authors used the Green's function technique in real space, which enabled us to calculate the excitation energy as well as the magnetization as a function of temperature. In the cases of the results presented in figure 12 the magnetic moment at the surface is slightly higher than in the middle of the particle and lower than in the interior of the particle. The fact of significant importance of the surface role finds experimental confirmation in the Mössbauer spectra of γ–Fe_2O_3 where the spectrum contains two components—one associated with the interior (bulk) of a particle and the second one associated with the atoms on the surface. The thickness of the surface region was estimated from the experiment as a layer of range thickness of 0.35 nm [29], that is, a range of less than two lattice constants.

The presented calculations show that the surface contribution to magnetization exhibits a different behavior than that of the core magnetization. Moreover, the local magnetic moment decreases with the increase of distance from the center of a particle. If we suppose that the value of the exchange constant is of the same value at the surface and in the interior of the material, the magnetization of the middle of a nanoparticle is higher than at the surface (figures 10 and 11).

The enhanced value of the exchange constant at the surface leads to a higher magnetic moment at the surface and the enhancement of the surface contribution as well as to a higher critical temperature of the considered system. Similar results were presented by Kachkachi *et al* [29] where the authors used the Monte Carlo technique for the nanoparticles of the simple cubic structure with different shapes.

The influence of the finite size effect on the critical temperature has been investigated experimentally for Co_3O_4 nanoparticles [30]. The obtained results show that the change of the critical temperature due to the geometrical confinement effect is proportional to $(1/R)^{1.1\pm0.2}$.

The importance of the size effect and as well as the surface effects was also confirmed in Monte Carlo simulation [33] for a model of a γ–Fe_2O_3 (maghemite) single particle [32]. A reduction of the magnetic ordering temperature, magnetization and coercive field is reported as the particle size is decreased. These facts can be interpreted as a consequence of the formation of a surface layer with a higher degree of magnetic disorder than that of the core which, for small sizes, dominates the magnetization process of the particle. The calculations confirm the role played by the surface.

Summing up, the size effect is important mainly for particles of diameters less than or equal $5.2a$ (a is the lattice constant) if we suppose that the exchange constant is $\frac{1}{5}J_b \leqslant J_s \leqslant 5J_b$. Moreover, the critical temperature of nanoparticles exhibits a strong dependence on the ratio J_s/J_b.

Appendix

A rigorous equation of state for solids, liquids and gases has been presented by Toop [1] for the PVT system. In particular, it reduces to the form of the van der Waals equation for gas. The thermodynamic relations connecting the pressure P, volume V and temperature T are well known in the literature [2] and can be written as

$$P = T\left(\frac{\partial P}{\partial T}\right)_V - \left(\frac{\partial U}{\partial V}\right)_T \tag{A.1}$$

$$V = T\left(\frac{\partial V}{\partial T}\right)_p + \left(\frac{\partial H}{\partial P}\right)_T \tag{A.2}$$

where U and H represent the molar energy and molar enthalpy, respectively.

(A.1) and (A.2) can be rewritten as follows:

$$P + \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V \tag{A.3}$$

and

$$V - \left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial V}{\partial T}\right)_p. \tag{A.4}$$

Multiplying (A.3) and (A.4) it is easy to obtain

$$\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left[V + \left(\frac{\partial H}{\partial P}\right)_T\right] = T^2\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p. \tag{A.5}$$

The term on the right-hand side of (A.5) can be written as

$$T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p = C_p - C_V. \tag{A.6}$$

Some comments should be made about the analogy between (A.5) and (A.6) which represents the van der Waals (vdW) equation:

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT. \tag{A.7}$$

The additional change of pressure is proportional to the number of pairs of interacting particles which are close to the wall of the reservoir while the effective volume is less than the whole volume of the system. Parameter b represents an excluded volume due to the hard core of the particles. Parameters a and b should be constant but for real gases they vary with P, V and T.

The vdW equation of state given by (A.7) tends to the equation of state for the ideal gas in the limit $V \to \infty$ for a fixed N.

Equation (A.7) can be obtained from (A.5) by setting in (A.5) $U = -\frac{a}{V}$ and $V - T\frac{\partial V}{\partial T} = V_0$. The last equation leads to

$$\frac{\mathrm{d}T}{T} = \frac{\mathrm{d}V}{V - V_0}. \tag{A.8}$$

The solution for V is of the following form:

$$V = V_0\left(1 + \frac{T}{T_0}\right) \tag{A.9}$$

where V_0 is the excluded volume of the system at temperature T_0.

The present derivation of the equation of state is of a general character, not only for the different types of interaction, but, first of all, for the systems which are described by the canonically conjugated variables.

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