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Theory and Computational Studies of Magnetic Carbon Nanotubes and of Depletion Effects in Colloid-Polymer Systems
by

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ABSTRACT

Theory and Computational Studies of Magnetic Carbon Nanotubes and of Depletion Effects in Colloid-Polymer Systems

by

Trinh Vo

Part I: *ab initio* Molecular Dynamics of Interaction of Fe Atoms with Single-Wall Carbon Nanotubes

The interaction of Fe atoms with a single-wall carbon nanotube is investigated using the *ab initio* molecular dynamics method of Car and Parrinello. The variations in stability, band gap, Fermi energy, and total magnetic moment of the Fe-single wall carbon nanotube systems are found to depend on the location of the Fe atoms relative to the carbon nanotube surface. Noteworthy is that the Fe atoms in the Fe-carbon nanotubes systems are coupled ferromagnetically. The curvature effects on the interaction of Fe atoms with carbon nanotubes are also studied by comparing with the Fe-graphite systems.

Part II: Phase Transitions and Long-Range Order of Magnetic Carbon Nanotubes

The magnetic coupling between single-wall carbon nanotubes filled with magnetic transition metals, which is assumed to be of the indirect type, is shown to lead to long-ranged ferromagnetic order for arrays of both metallic and semiconducting carbon nanotubes. The critical temperature and spontaneous magnetization are determined. It is
found that metallic and semiconducting carbon nanotubes filled with magnetic elements can be turned into magnetic materials.

Part III: Computer Simulation of Depletion Effects in Three-Dimensional Colloid-Polymer Systems

The phase behavior of three-dimensional colloid-polymer systems with purely depletion-induced attractions (hard chain polymer and hard sphere colloid) is studied using finite-size scaling and histogram-reweighting Monte Carlo simulations. The nature of the coexisting phases and the phase diagrams are found to depend on the polymer-to-colloid size ratio $q$. The threshold values of $q$ where liquid-liquid coexistence disappears are found to differ significantly from the value predicted by mean-field theories. Phase separation is found to occur at the "protein limit" of very large polymer and small colloids, in contrast to de Gennes' prediction.

Part IV: Depletion Interaction in One Dimension: Short-Range Order

For one-dimensional systems in the continuum in which the particles interact with nearest-neighbor forces, the pair correlation function at short distances can be expressed exactly in a simple form. Results are given for the hard-core interaction potential in which the attractive potential is linear, which represents the depletion interaction potential in one dimension.
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# List of Symbols

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<td>$c_i^k$</td>
<td>Fourier component</td>
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<tr>
<td>$D_{C,Fe}$</td>
<td>Bond length or distance between C and Fe atoms</td>
</tr>
<tr>
<td>$D_{Fe,Fe}$</td>
<td>Bond length or distance between Fe and Fe atoms</td>
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<td>Mass of nucleus</td>
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</table>
\( r, \ r \) Coordinates of electrons

\( R_h, R_I \) Coordinates of nuclei

\( t \) Time

\( U \) Coupled potential energy between electrons and nuclei

\( w_k \) k-point weight

\( z \) Distance from an iron atom to the CN or graphene surface

\( Z \) Ion charge

\( \alpha \) Constraint

\( \Delta E_g \) Band gap difference

\( \Delta E_F \) Fermi energy difference

\( \Lambda \) Lagrange multiplier

\( \mu \) Fictitious mass

\( \mu_M \) Total magnetic moment

\( \mu_B \) Bohr magneton

\( v_{NL} \) Non-local potential

\( \Omega \) Volume

\( \rho_e \) Electron density

\( \rho_l \) Smeared charge distribution

\( \Psi \) Wave function

**Part II**

\( A \) C-C bond length

\( B_S, B_I \) Brillouin function
\( e \) Charge

\( E \) Energy

\( E_g \) Band gap energy

\( g \) Lande factor or spectroscopic splitting factor

\( \hbar \) Planck constant

\( \mathcal{H} \) Hamiltonian

\( \mathbf{H}_e \) Effective field

\( \mathbf{H}_0, \mathbf{H} \) Applied magnetic field

\( \mathbf{J} \) Total orbital angular momentum (only in Sections 5.1 to 5.2)

\( j \) Eigenvalue of \( \mathbf{J} \) (only in Sections 5.1 to 5.2)

\( J \) Exchange interaction

\( J_{\text{direct}} \) Direct exchange interaction

\( J_{\text{indirect}} \) Indirect exchange interaction

\( \mathbf{J} \) Exchange integral between an electron of the magnetic shell and a conduction electron

\( k \) Wave vector

\( k_B \) Boltzmann constant

\( L \) Total orbital angular momentum

\( L \) Eigenvalue of \( L \)

\( L_z \) Eigenvalue of \( L \) in \( z \)-direction

\( m_e \) Electron mass

\( m^* \) Effective electron mass

\( \mathbf{M}, M \) Magnetization
$M_0$  Saturated magnetization

$n(T)$  Conduction electron density

$N$  Total number of atoms per unit cell

$r$  Distance between two magnetic ions

$S$  Spin angular momentum

$S$  Spin

$T$  Temperature

$T_c$  Critical temperature

$V$  Unit cell Volume

$z$  Coordination number

$\eta$  Degeneracy of the electron gas

$\gamma_o$  Energy overlap integral

$\lambda$  Coupling constant or molecular field parameter

$\mu$  Total magnetic moment

$\mu_h$  Magnetic moment

$\mu_s$  Spin magnetic moment

$\theta$  Paramagnetic Curie temperature

$\Omega$  Volume of atomic cell

$\chi$  Susceptibility

**Part III**

$A$  Nonuniversal constant

$E$  Total configuration energy
\( f(N,E) \) Frequency of occurrence of \( N \) particles with total configurational energy \( E \)

\( L \) Box length

\( M \) Ordering operator

\( M_c \) Critical value of ordering operator

\( N \) Total number of particles

\( N_i \) Total number of particles \((i = 1, 2\) for components 1 and 2, respectively or \( i = c, p \) for colloid and polymer, respectively\)

\( n \) Number of monomer in a polymer chain

\( P \) Probability distribution

\( P_L \) Probability distribution for a fixed box length of \( L \)

\( q \) Ratio of polymer radius of gyration to colloidal radius

\( R_g \) Radius of gyration of polymer

\( s \) Field-mixing parameter (for the number of component 1)

\( u \) Field-mixing parameter (for the number of component 2)

\( T \) Temperature

\( T_c \) Critical temperature

\( V \) Volume

\( \alpha \) Exponent associated with heat capacity

\( \Phi_c \) Volume fraction of colloid \((\Phi_c = \rho_c \frac{4}{3} \pi \sigma^3)\)

\( \Phi_p \) Volume fraction of polymer \((\Phi_p = \rho_p \frac{4}{3} \pi R_g^3)\)

\( \eta_p \) Volume fraction of polymer \((\eta_p = nN_p / V)\)

\( \eta_p^* \) Critical volume fraction of polymer
\(\mu\)  Chemical potential

\(\mu_c\)  Chemical potential of colloid

\(\mu_p\)  Chemical potential of polymer

\(\nu\)  Correlation length exponent

\(\rho_c\)  Colloidal density

\(\rho_{c*}\)  Critical density of colloid

\(\rho_{\text{crit}}\)  Critical density

\(\rho_p\)  Number density of polymer (number of polymer chains per volume)

\(\theta\)  Correlation-to-scaling exponent

\(\sigma\)  Colloidal diameter

\(q_{th}\)  Threshold value of \(q\) at which liquid-liquid coexistence disappears

\(\tau\)  Thermal transform

\(\tau^*\)  Critical thermal transform (\(\tau = -1/\mu_c\))

\(\Omega\)  Microcanonocal partition function

\(\Xi\)  Grand canonical partition function

**Part IV**

\(\alpha\)  Particle diameter

\(N\)  Number of particles

\(L\)  Length

\(r\)  Coordinate

\(R_i\)  Coordinate of particle \((i = 1, 2, \ldots)\)

\(\varepsilon\)  Depth of potential energy (potential minimum)
\[ \Phi_N \] Total potential energy

\[ \Phi \] Interaction potential between nearest-neighbor particles \( i \) and \( j \)

\[ \lambda \] Range of interaction (attraction)

\[ \rho^{(1)}(r) \] Average number density

\[ \rho^{(2)}(r) \] Average number density of ordered pairs
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BG</td>
<td>Fe atom is above the center of C-C bond of graphene sheet</td>
</tr>
<tr>
<td>BO</td>
<td>Born-Oppenheimer</td>
</tr>
<tr>
<td>BZ</td>
<td>Brillouin zone</td>
</tr>
<tr>
<td>CN</td>
<td>Carbon nanotube</td>
</tr>
<tr>
<td>CP</td>
<td>Car-Parrinello</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>FC</td>
<td>Fourier component</td>
</tr>
<tr>
<td>FP</td>
<td>First principle</td>
</tr>
<tr>
<td>GGA</td>
<td>Graduated Gradient Approximation</td>
</tr>
<tr>
<td>HG</td>
<td>Fe atom is at the hole position above graphene sheet</td>
</tr>
<tr>
<td>IB1</td>
<td>Symmetric bond (Fe atom is inside the tube and above the center of the C-C bond parallel to the tube axis)</td>
</tr>
<tr>
<td>IB2</td>
<td>Asymmetric bond (Fe atom is inside the tube and above the center of the C-C bond along the radial direction)</td>
</tr>
<tr>
<td>IH</td>
<td>Fe atom is at the hole position inside a CN</td>
</tr>
<tr>
<td>IT</td>
<td>Fe is inside the tube and above a C atom</td>
</tr>
<tr>
<td>KS</td>
<td>Kohn Sham</td>
</tr>
<tr>
<td>LDA</td>
<td>Local Density Approximation</td>
</tr>
<tr>
<td>MC</td>
<td>Monte Carlo</td>
</tr>
<tr>
<td>MD</td>
<td>Molecular Dynamics</td>
</tr>
<tr>
<td>OH</td>
<td>Fe atom is at the hole position outside a CN</td>
</tr>
</tbody>
</table>
OB1  Symmetric bond (Fe atom is outside the tube and above the center of the C-C bond parallel to the tube axis)

OB2  Asymmetric bond (Fe atom is outside the tube and above the center of the C-C bond along the radial direction)

OT   Fe is outside the tube and above a C atom

PP   pseudopotential

PW   Plane wave

PBC  Periodic boundary condition

TG   Fe atom above the C atom of graphene sheet

SWCN Single-wall carbon nanotube

Part II

RKKY Ruderman-Kittel-Kasuya-Yosida

Part III

GEMC Gibbs ensemble Monte Carlo

MC   Monte Carlo
Part I

*ab initio* Molecular Dynamics of Interaction of Fe Atoms

with Single-Wall Carbon Nanotubes
Chapter 1: Introduction

The discovery of carbon nanotubes (CN) has opened new areas for research. A carbon nanotube can be formed by rolling up a graphene sheet into a cylindrical shape. In spite of being simple in structure, carbon nanotubes have many attractive properties: they are ultrastrong, chemically inert, flexible, and have diverse electronic transport properties (they can be metallic or semiconducting, depending on their diameter and chirality). Consequently, CN's are promising candidates for several technical applications ranging from composites, photonics, quantum dots, to nanoelectronic devices such as field-effect transistors and spintronics. In such applications, CN's are usually used as constructing building blocks for the devices by themselves, or in combination with other elements.

CN's are themselves diamagnetic materials. Therefore, one question can be raised: Can CN's be made ferromagnetic? One of the proposed routes to make new magnetic materials based on CN's is to couple the single-wall carbon nanotubes (SWCN) with magnetic transition or rare-earth metals. Before attaining this goal, there are many other questions that need to be answered: Is the process of combining CN's with magnetic transition metals favorable in energy? What are the electronic structures of the combined
systems? Is there a modification in electronic properties of CN’s? What are the magnetic properties of the new materials? In the following, carbon nanotubes will always be assumed to be single-wall nanotubes, and they will most often be denoted for simplicity by CN rather than SWCN.

Study of the physical properties as well as of the electronic structures of transition metal atoms adsorbed on a SWCN is of current interest from both fundamental and practical points of view in nanoscience and nanotechnology. First, knowing the electronic structures and metal-tube interaction of a system of CN’s filled with magnetic transition metals is very helpful in studying magnetic properties in low dimensions. Second, magnetic transition metals (such as Fe, Co, Ni) are used as catalysts for the synthesis of CN’s, but the key role of transition metals in the synthesis of carbon nanotubes is not well understood. In nanoelectronic applications, understanding the interaction between the metals and CN’s also plays an important role in making devices having low resistance contact between metals and CN’s, as well as in other issues such as forming metals or superconducting nanowires on nanotube templates. In those cases, the bonding between CN’s and metals depends on the detailed contact conditions, and careful studies are required to shed light into these issues.

Recently, a few experimental and theoretical works related to magnetic transition metals interacting with SWCN’s have been reported in the literature. Dujardin et al showed that Ni used in the synthesis of SWCN remains in purified samples even after prolonged treatment in boiling concentrated HNO. They also observed an even distribution of small clusters or isolated atoms of these transition metals within the nanotubes. Andriotis et al indicated from their calculations on the system of Ni and
SWCN that contact resistance in SWCN sensitively depends on the bonding configurations of transition metal atoms on the nanotubes. Menon et al.\textsuperscript{12} used tight binding molecular dynamics to study the interaction of Ni with a SWCN and found that the interaction depends on the tube curvature. Their predicted values of the binding energy between a Ni atom with a SWCN are however too large and become questionable, requiring a more accurate calculation. Furthermore, all tight binding methods are semi-empirical, and the results depend on the chosen values of the parameters, which are obtained from either experiments or other calculations.

In this thesis, in order to understand and answer the questions and problems raised above, the structural, electronic, and magnetic properties of a system of carbon nanotubes and Fe atoms are systematically investigated using the \textit{ab initio} molecular dynamics Car-Parrinello method combined with ultrasoft pseudopotentials.\textsuperscript{15} We study Fe-CN interactions for various configurations of a single Fe atom, of Fe clusters, and of a chain of Fe atoms inside and outside carbon nanotubes of various sizes. The effect of curvature is also considered by comparing the results of a carbon nanotube containing Fe atoms with those of Fe atoms adsorbed on a sheet of graphite (graphene).
Chapter 2: \textit{ab-initio} Molecular Dynamics

Classical molecular dynamics using "predefined potentials," either based on empirical data or on independent electronic structure calculations, is well-established as a powerful tool to investigate many-body condensed matter systems. However, at the very heart of any molecular dynamics is the question of how to describe -that is, in practice, how to approximate- the interatomic interaction potentials. The traditional route is to determine these potentials in advance by breaking up the potentials into two-body, three-body and many-body contributions, and into long-range and short-range terms, etc. After decades of intense research, very elaborate interaction models have been devised.

Despite overwhelming success, the need to devise a "fixed model potential" implies serious drawbacks. Among the most delicate ones are those of systems where (i) many different atom or molecule types give rise to a myriad of different interatomic interactions that have to be parametrized and/or (ii) the electronic structure and thus the bonding pattern change qualitatively in the course of the simulation. These systems can be called "chemically complex."

The reign of traditional molecular dynamics and electronic structure methods was greatly extended by the family of techniques called "\textit{ab initio} molecular dynamics."
Other names are currently in use, for instance Car-Parrinello, Hellmann-Feymann, first principles, quantum chemical, on-the-fly, etc. The basic idea underlying every *ab initio* molecular dynamics method is to compute the force acting on the nuclei from electronic structure calculations that are performed “on-the-fly” as the molecular dynamics trajectory is generated. In this way, the electronic variables are not integrated out beforehand, but are considered as active degrees of freedom. This implies that, given a suitable approximate solution of the many-electron problem, also “chemically complex” systems can be handled by molecular dynamics. This also implies that the approximation is shifted from the level of selecting the model potential to the level of selecting a particular approximation for solving the Schrödinger equation.

In the next section the Car-Parrinello method and its practical implementation are described.

### 2.1 Car-Parrinello Method

The basic idea of the Car-Parrinello\(^{15}\) (CP) method is the combination of both molecular dynamics (MD) and density-functional theory (DFT). MD is a well-established methodology for the calculation of statistical properties of condensed matter systems. The essence of the method is the numerical solution of Newton’s equations of motion for the ensemble of atoms. These equations are solved with iterative techniques for appropriately long times, and equilibrium statistical averages are computed as temporal averages over the observation time. In conventional MD, the interactions between atoms are modeled with empirical potentials. Although many systems have successfully been investigated with model potentials, it is difficult to find empirical
interactions which work for different states of matter and for a wide class of materials. The MD approach may especially fail for covalent and/or metallic systems. Furthermore, this approach conveys no information about electronic properties such as the correlation between local atomic structure, atomic dynamics, and the effect of the atomic dynamics on the electronic properties. DFT, on the other hand, deals with the ground state of a quantum-mechanical many-body system of electrons. In principle, it provides an accurate description of chemical bonding in a large variety of systems. However, it is computationally demanding, and this has so far precluded its application to the study of very large and/or disordered systems, as well as to the computation of interatomic forces for MD simulations.

The unified approach to DFT and MD suggested by Car and Parrinello is able to overcome these difficulties and to achieve the following results: (i) compute ground-state electronic properties of large and/or disordered systems at the level of state-of-the-art electronic structure calculations; (ii) perform \textit{ab initio} MD simulation where the only assumptions are the validity of classical mechanics to describe ionic motion and the Born-Oppenheimer (BO) approximation to separate nuclear and electronic coordinates.

According to Kohn and Sham (KS), the electron density in terms of occupied single-particle orthonormal orbitals is\textsuperscript{16}

$$\rho_e(r) = \sum_i |\psi_i(r)|^2.$$  

(1.1)

A point of the BO potential energy surface is given by the minimum of the energy density functional with respect to $\psi_i(r)$,\textsuperscript{15}

$$E[\{\psi_i\}, \{R_i\}, \{\alpha_v\}] = \sum_i \int_\Omega \left[ d^3r \psi_i^*(r) \left( -\frac{\hbar^2}{2m} \right) V^2 \right] \psi_i(r) + U[\rho_e(r), \{R_i\}, \{\alpha_v\}].$$  

(1.2)
Here \( \{R_i\} \) indicates the nuclear coordinates and \( \{\alpha_i\} \) are all the possible external constraints imposed on the system, such as the volume \( \Omega \). The functional \( U \) contains the internuclear Coulomb repulsion and the effective electronic potential energy, including external nuclear, Hartree, and exchange and correlation contributions.

In the conventional formulation, minimization of the energy functional [Eq. (1.2)] with respect to the orbital \( \psi_i \), subject to the orthonormality constraint, leads to the self-consistent KS equations, i.e., to

\[
- \frac{\hbar^2}{2m} \nabla^2 \psi_i(r) + \frac{\delta U}{\delta n(r)} \psi_i(r) = \epsilon_i \psi_i(r). \tag{1.3}
\]

The solution of Eq. (1.3) involves repeated matrix diagonalizations with a computational effort rapidly growing with the size of the system. Since the whole procedure has to be repeated for any new atomic configuration, the theoretical prediction of the equilibrium geometries, when those are not known form experiment, still remains an unsolved problem in most cases.

Car and Parrinello\(^{15}\) suggested a different approach: the minimization of the KS functional as a complex optimization problem, which can be solved by applying the concept of simulated annealing proposed by Kirkpatrick, Gelatt, and Vecchi.\(^{17}\) In this approach, an objective function \( O(\{\beta\}) \) (to be defined below) is minimized relative to the parameter \( \{\beta\} \), by generation of a succession of \( \{\beta\}'s \) with a Boltzmann-type probability distribution proportional to \( \exp[O(\{\beta\})/T] \), via a Monte Carlo procedure. For \( T \to 0 \), the state of lowest \( O(\{\beta\}) \) is reached unless the system is trapped into some metastable state.

In the CP approach,\(^{15}\) the objective function is the total-energy functional, and variational parameters are the coefficients of the expansion of the KS orbitals in some
convenient basis (in this case, plane-wave basis sets and pseudo potentials, which are described in the next section) and possibly the ionic positions and/or the $\alpha_{i,j}$'s. Car and Parrinello also found that a simulated annealing strategy based on MD, which they named later "dynamical simulated annealing," rather than on the Metropolis Monte Carlo method of Parrinello Kirkpatrik, Gelatt, and Vecchi, 17 could be applied efficiently to minimize the KS functional.

The key point in the first-principle molecular dynamics method proposed by Car and Parrinello is the definition of a fictitious dynamical system, associated with the physical system, whose potential energy surface $E$ is an appropriate functional of both ionic and electronic degrees of freedom; the fictitious system is devised in such a way that the trajectories generated by its dynamics reproduce very closely the potential energy surface $v$. According to their method, the generalized classical Lagrangian of the fictitious system is defined as $^{15}$

$$L = \sum_{i}^{\text{occ}} dr \mu_{i} \left| \psi_{i}(r) \right|^{2} + \frac{1}{2} \sum_{i} M_{i} \dot{R}_{i}^{2} - E[\{\psi_{i}\}, R_{i}] + \sum_{i,j} \Lambda_{i,j} \left( \int dr \psi^{*}_{i}(r) \psi_{j}(r) - \delta_{ij} \right). \quad (1.4)$$

$L$ does not depend explicitly on time, and is a functional of two sets of classical degrees of freedom, $\psi_{i}$ and $R_{i}$, which depend on time. The $\mu_{i}$ ("fictitious mass") are arbitrary parameters of units (mass)$x$(length)$^{2}$, which play the role of generalized masses for the electronic degrees of freedom; how to choose these parameters remains to be specified. The first and the second terms in the Lagrangian [Eq. (1.4)] are the kinetic energy of the electronic and ionic degrees of freedom, $K_{e}$ and $K_{i}$, respectively. $E$ is the potential energy of the coupled electron-ion fictitious system. The Lagrange multipliers $\Lambda_{i,j}$ are
used to impose orthonormality conditions on the \( \psi_i \); in the language of classical mechanics, they are just simple holonomic constraints.

The Lagrangian of Eq. (1.4) generates the dynamics for the parameters \( \{\psi_i\} \)'s and \( \{R_i\} \)'s through the equations of motion:\(^{15}\)

\[
\mu \ddot{\psi}_i (r, t) = -\frac{\delta E}{\delta \psi_i} + \sum_k \Lambda_{ik} \psi_k (r, t) ,
\]

\[
M_i \ddot{R}_i = -\nabla_{R_i} E .
\]

The ion dynamics in Eq. (1.5) may have a real physical meaning, whereas the dynamics associated with the \( \{\psi_i\} \)'s is fictitious and has to be considered as a tool to perform the dynamical simulated annealing. The parameter \( \mu \) and the initial conditions \( \{\psi_i\}_0, \{\psi_i\}_0 \) can be chosen so that the two sets of classical degrees of freedom, ions and electrons, are only weakly coupled, and the transfer of energy between them is small enough to allow the electrons to follow the ionic motion, remaining close to the BO surface. In such a metastable situation, meaningful temporal averages can be computed. This dynamics, which is called classical adiabatic dynamics,\(^{18}\) is meant to reproduce in a computationally effective way what indeed occurs in real life; that is, electrons following adiabatically the motion of ions. The role of Eq. (1.5a) is to keep the electrons on the BO surface, without solving self-consistently the KS equations at each step, but only for the initial configuration.

It is also noted that by variation of the velocities \( \dot{\psi}_i \) and \( \dot{R}_i \), one can vary the temperature of the system, thus making the fictitious dynamical system undergo various thermal treatments, such as annealing and quenching. During such processes, all the
relevant degrees of freedom, both nuclear and electronic, are relaxed simultaneously. In particular, one can set up a dynamical process that brings the system to its equilibrium state at $T = 0$ by slowly reducing the ionic temperature (such a process is called dynamical simulated annealing). At equilibrium, $\dot{\psi}_i = 0$, and Eq. (1.5) is identical, within a unitary transformation, to the KS equation [Eq. (1.2)], and the eigenvalues of the matrix $\Lambda$ coincide with the occupied KS eigenvalues. Only when these conditions are satisfied does the Lagrangian in Eq. (1.3) describe a real physical system whose representative points in configurational space lies on the BO surface. The Car-Parrinello scheme is found to be more efficient than standard diagonalization techniques.\textsuperscript{15} Furthermore, in this approach, diagonalization, self-consistency, ionic relaxation, and volume and strain relaxation are achieved simultaneously. The amount of classical kinetic energy is a measure of the departure of a system from the self-consistent minimum of its total energy.

2.2 Practical Implementation of the \textit{ab-initio} MD Scheme

2.2.1 Basis Sets for the Electronic Orbitals and MD Supercells

The first-principle molecular dynamics scheme (FP-MD) just described in Section 2.1 was originally based on a pseudopotential (PP) description of the interaction between ionic cores and valence electrons, in conjunction with plane-wave (PW) basis sets.\textsuperscript{15} The choice of PW expansions for the single-particle orbitals has several advantages. The mathematical formulation is particularly simple. The basis set is independent of the ionic positions, in contrast to the Gaussian basis sets, giving an unbiased uniform description of the simulation cell and preventing undesirable Pulay terms\textsuperscript{19} from appearing in the
calculation of ionic forces. PW's easily allow the use of fast Fourier transform (FFT's) to transfer quantities from real space to Fourier space, and vice versa. Another advantage is the possibility of testing the accuracy of the results by increasing the energy cutoff, which defines the highest kinetic energy of the waves in the basis set.

The disadvantage of the PW expansions is the very large number (M) of basis functions needed to represent the electronic orbitals compared, for example, to basis sets of Gaussian or atomic-like orbitals. PW basis sets call for the use of pseudopotentials, since the number of PW's needed to describe localized core states is too large and cannot be afforded from the computational point of view.

In simulations of bulk systems, the MD box is periodically repeated to infinity. This is a natural choice for perfect crystals, whose Hamiltonian possesses translational symmetry.\(^{18}\) For disordered systems, such as amorphous solids or liquids, periodic boundary conditions (PBC) can still be adopted, provided that the MD box is chosen large enough so that the imposed periodicity does not affect the dynamical properties of the system.

As a consequence of the periodicity introduced by PBC, the single-particle orbitals entering the Lagrangian [Eq. (1.4)] satisfy the Bloch theorem and can be expanded in PW's:\(^{18}\)

\[
\psi^k_i(r) = e^{i k \cdot r} \sum_g c^k_i(g) \ e^{i g \cdot r}, \tag{1.6}
\]

where \(g\) is a reciprocal lattice vector of the MD supercell, and the wave vector \(k\) lies within the Brillouin Zone (BZ) of the reciprocal lattice of the supercell. \(c^k_i(g)\) are the Fourier components (FC) of the single-particle wavefunction, which are treated as time-dependent degrees of freedom in the calculation. The basis set specified in Eq. (1.6) is
reduced to a finite set by truncating the sum over $g$ to include only those plane waves with a kinetic energy $E_k = \frac{1}{2} (k + g)^2$ less than a given energy $E_{\text{cut}}$. The value of $E_{\text{cut}}$ depends on the specific system and in particular upon the choice of the pseudopotential for the description of the core-valence interaction. For a given pseudopotential the choice of $E_{\text{cut}}$ determines the accuracy of the calculation.

The computation of the electronic density ($\rho_e(r)$) and then of the total energy requires an integral over the BZ:

$$\rho_e(r) = \sum_k w_k \sum_i |\psi_i^+(r)|^2,$$  \hspace{1cm} (1.7)

where $w_k$ is the $k$-point weight. In principle, an infinite number of points should be included in the summation in Eq. (1.7). In practice, an appropriate small set, chosen according to the symmetry properties of the $\rho_e(r)$, leads to a rapid convergence of the summation.

2.2.2 Pseudopotentials

In most molecular or solid-state systems, it is possible to separate atomic states into valence states, which determine the bonding properties, and core states which are much deeper in energy and can therefore be considered as chemically inert. In the pseudopotential (PP) scheme, the electronic problem is simplified by considering only the valence states. Note that the separation between valence and core states is not strict, and it is even possible that for the same kind of atom the number of valence states changes according to the environment or to the degrees of approximations allowed. The core states are considered essentially unchanged with respect to the free atom and affect the valence wave functions only through the orthonormality condition. These inert states can
be eliminated by replacing the true atomic Coulomb potential by PP's, designed in such a way that the effect of the core states is effectively reproduced. It is noted that the PP needs to give an accurate description of the core-valence interaction only in a finite energy range, in order to correctly reproduce the bonding properties of a given system.

In the original CP version, norm-conserving PP's (Refs. 20 and 21) have been used in their fully separable form. In such a PP scheme, the pseudo-wave-function matches the all-electron wave function beyond a cutoff radius which defines the core region. Within the core region, the pseudo-wave-function has no nodes and is related to the all-electron wave function by the norm-conserving condition which ensures that both wave functions carry the same charge. In addition, the PP to be used with in conjunction with PW basis set is to be as smooth as possible, e.g., to achieve the lowest possible $E_{\text{cut}}$. In the spirit of reducing the energy cut-off, several improvements have been proposed. However, despite these improvements, the energy cutoff needed to describe the localized valence orbitals of first-row elements or transition metals is still frequently too high to allow MD simulations of extended systems.

Vanderbilt has proposed a new PP scheme in which the norm-conserving condition on the pseudo-wave-functions has been relaxed. The associated PP's are termed \textit{ultrasoft}. In this scheme, the pseudo-wave-functions are allowed to be as soft as possible within the core region, yielding a dramatic reduction of the cutoff energy required to describe them. Technically, this is accomplished by introducing a generalized orthonormality condition, which modifies the conventional approach significantly. In order to recover the full electronic charge, the electron density given by the squared moduli of the wave functions is augmented in the core regions. Thus, the electron density can be subdivided in a
Fig. 2.1. All-electron (solid) and pseudo (dashed) radial wave function of the 3d orbital of Cu. A cutoff radius of 2 a.u. has been used (from Ref. 27).

smooth part extending throughout the unit cell, and a hard part localized in the core regions. In Fig. 2.1, the result of this procedure in the case of the 3d-orbital of Cu is illustrated. The radial-all-electron wavefunction has no node, since it is the lowest state of d symmetry. Therefore, the use of pseudo potential is particularly effective in this case.
2.2.3 Energy and Forces with Norm-Conserving Pseudopotentials

Fig. 2.2 outlines the basic steps of an ab-initio MD simulation.\textsuperscript{18} At $t = 0$ the ground-state single-particle orbitals $\psi_i$ associated with the electronic states of the system in a chosen initial ionic configuration have to be provided. The total energy and its derivatives with respect to the ionic positions can then be computed. The action of the Hamiltonian on each Fourier component (FC) is evaluated in order to solve the equation

$$\mu \ddot{\psi}_i = -H_{\text{FC}} \psi_i \quad (1.8)$$

for each vector $k$ and electronic state $i$. Eq. (1.8) does not contain the forces coming from the orthogonality constraints that the wavefunctions must satisfy. These are accounted for in a subsequent step where the electronic states are orthogonalized. When both electronic and ionic degrees of freedom are evolved in time according to the second-order equations of motion (EOM) and a MD run is performed, the choice of the orthogonalization procedure is crucial and has to be appropriate for the treatment of holonomic constraints. After solving the EOM for the electronic degrees of freedom, one solves those for the ionic degrees of freedom. Finally, the time step is incremented and the new positions from Eq. (1.5b) and new positions from Eq. (1.8) are used as input for the next step.

The total energy $E$ is given by the sum of the Hohenberg-Kohn energy functional and of the ion-ion interaction energy $E_M$:\textsuperscript{18}

$$E = E_k + E_{xc} + E_H + E_{ps} + E_M \quad (1.9)$$

where

$$E_M = \frac{1}{2} \sum_{i \neq j} \frac{Z_i Z_j}{|R_i - R_j|} \quad (10)$$
Fig. 2.2. The flow chart of an *ab-initio* molecular dynamics run (from Ref. 18)
The kinetic energy of the electrons, $E_k$, is evaluated in Fourier space:

$$E_k = \frac{1}{2} \sum_{i,j} g^2 c_i^*(g)c_j(g). \quad (1.11)$$

$E_H$ and $E_{ps}$ denote the Hartree and pseudopotential energy, respectively:

$$E_{ps} = \int dr \, v(r) \rho_e(r). \quad (1.12)$$

where $v(r)$ is the total ionic potential acting on electrons, and $\rho_e$ is the electron density. $E_{ps}$ is further split into two contributions, a local ($E_{ps}^L$) and a non-local ($E_{ps}^{NL}$) one:

$$E_{ps}^L = \int dr \rho_e(r) \sum_I v_{loc}(\mid r - R_I \mid). \quad (1.13)$$

where $v_{loc}$ is the local part of the pseudopotential, and

$$E_{ps}^{NL} = \sum_I \langle \psi_i | v_{NL} | \psi_i \rangle, \quad (1.14)$$

where $v_{NL}$ is the non-local part of the pseudopotential given by

$$v_{NL} = \sum_I \sum_{l=0}^{l-1} \Delta v_l (\mid r - R_I \mid \hat{P}_l(R_I)). \quad (1.15)$$

Here the operator $\hat{P} (R_I)$ is the projector on the $l^{th}$ angular momentum with respect to the point $R_I$. As far as $E_M$ is concerned, it is convenient to replace the ionic core point charge by smeared charge distributions $\rho_l$, e.g., Gaussian centered at the ionic sites:

$$\rho_l(r - R_I) = -\frac{Z_l}{(R_I^c)^3} (\pi)^{3/2} \exp \left( -\frac{\mid r - R_I^c \mid^2}{(R_I^c)^2} \right). \quad (1.16)$$

$R_i^c$ determines the width of the Gaussian distribution associated with site $I$. The term $E_M$ then can be written as follows:
\[ E_M = \frac{1}{2} \sum_{I,J} \int dr \, dr' \, \frac{\rho_I (r - R_I) \rho_J (r' - R_J)}{|r - r'|} - E_{self} - E_{ovrl}, \quad (1.17) \]

where the sum runs over all \( I \) and \( J \). The term \( E_{self} \) is the self-interaction of the smeared charge:

\[ E_{self} = \frac{1}{\sqrt{2\pi}} \sum_{I} \frac{Z_I^2}{(R_I^c)^2}. \quad (1.18) \]

The term \( E_{ovrl} \) accounts for the difference between the original point-charge interactions and the interactions between smeared charges:

\[ E_{ovrl} = \frac{Z_I Z_J}{R_{IJ}} \text{erfc} \left( \frac{R_{IJ}}{\sqrt{(R_I^c)^2 + (R_J^c)^2}} \right), \quad (1.19) \]

where \( R_{IJ} = |R_I - R_J| \).

On performing the summation of the three terms \( E_M, E_H \) and \( E_{ps} \), one obtains\(^{18}\)

\[ E_M + E_H + E_{ps} = \frac{1}{2} \int dr \, dr' \, \frac{\rho(r) \rho(r')}{|r - r'|} + \int dr \, \rho_s (r) \sum_I v_{loc}^I (r - R_I) - E_{self} - E_{ovrl}, \quad (1.20) \]

where \( \rho = \rho_s + \rho_I \), and \( v_{loc} \) is local part of pseudopotential

\[ v_{loc}^I (r) = \left[ v_{loc} (r) - \frac{Z_I}{r} \text{erfc} \left( \frac{r}{R_I^c} \right) \right]. \quad (1.21) \]

The remaining term \( E_{ps}^L \) can be written as\(^{18}\)

\[ E_{ps}^{NL} = \sum_i \sum_{g, g'} e^{-i g * R_i} c_i^* (g) v_{NL} (g, g') c_i (g'), \quad (1.22) \]

where

\[ v_{NL} (g, g') = 4\pi \sum_{l=0}^{l-1} (2l + 1) P_l [\cos (\theta_{gg'})] \int dr \, r^2 \, j_i (gr) j_i (g'r) \Delta v_l (r). \quad (1.23) \]
$P_l$ is the Legendre polynomial of order $l$; $j_l$ denotes a spherical Bessel function of the first kind of order $l$, and $\theta_{gg'}$ is the angle between $g$ and $g'$. In principle, $[N_k \cdot N \cdot N_{\text{at}} \cdot M(M + 1)/2]$ integrals of the kind entering Eq. (1.22) are needed in order to compute $E^L_{ps}$, where $N_k$ is the number of points used to sample the BZ and, as usual, $M$, $N$, and $N_{\text{at}}$ are the number of basis functions, electronic states, and atoms, respectively. This usually amounts to a very large number of integrals, making the evaluation of $E^L_{ps}$ computationally very demanding.

### 2.2.4 Energy and Forces with Ultrasoft Pseudopotentials

The ultrasoft PP proposed by Vanderbilt$^{28}$ can efficiently be implemented in a first-principle MD scheme in general and in the CP method$^{27}$ in particular. As a consequence of the generalized orthonormality condition (see Section 2.2.2), the calculations are affected in several ways. First, a new term appears in the Kohn-Sham equations which depends on the wave functions and thus must be updated at every time step. Second, the orthonormality condition depends on the ionic positions. As a consequence, the manner in which this condition is imposed during the ionic motion and the expressions for the ionic forces are substantially modified in comparison to the norm-conserving case. Finally, the hard core contribution to the electron density must be accounted for without losing the advantage of the low cutoff energy required for the wave function.

The total energy $E$ is given by the same expression as in the norm-conserving case, Eq. (1.9), where the non-local contribution to the pseudopotential is $v_{\text{NL}}$ given by

$$v_{\text{NL}} = \sum_{nm, l} D^0_{nm} \left| \beta^l_n \right\langle \beta^l_m \left| . \right.$$  

(1.24)
The function $\beta_n^I$ and the coefficient $D_{nm}^0$ characterize the PP and differ for different atomic species. For one atomic species, the functions $\beta_n^I$ are centered on site $I$, related to the atomic functions $\beta_n$ by

$$
\beta_n^I (r) = \beta_n (r - R_I). \tag{1.25}
$$

Here $\beta_n$ is an angular momentum eigenfunction in the angular variables, times a radial function which vanishes outside the core region; the indices $m$ and $n$ run over the total number $N_\beta$ of such functions.

The electron density is given by

$$
\rho_e(r) = \sum_i |\phi_i(r)|^2 + \sum_{m,n,I} Q_{nm}^I (r) \langle \phi_i | \beta_n^I \rangle \langle \beta_m^I | \phi_i \rangle, \tag{1.26}
$$

where the augmented functions $Q_{nm}^I (r) = Q_{nm} (r - R_I)$ are also provided by the PP and are strictly localized in the core regions. Thus, while the electron density in Eq. (1.26) is still quadratic in the wave functions, it is now separated into a soft delocalized contribution given by the squared moduli of the wave functions, and a new hard contribution localized at the core.

The relaxation of the norm-conserving condition is achieved by introducing a generalized orthonormality condition

$$
\langle \phi_i | S(\{R_I\}) | \phi_i \rangle = \delta_{ij}, \tag{1.27}
$$

where $S$ is a Hermitian overlap operator given by

$$
S = 1 + \sum_{n,m,I} q_{nm} |\beta_n^I \rangle \langle \beta_m^I |, \tag{1.28}
$$

and where $q_{nm} = \int dr q_{nm} (r)$.
The functional derivative is modified, with respect to the norm-conserving scheme, as follows

\[
\frac{\delta E}{\delta \psi^*_{i}} = \left[ -\nabla^2 + \sum_{nn,l} D^l_{nm} \beta_n \beta_m \right] \psi_i = \epsilon_i S \psi_i ,
\]

(1.29)

where \( \epsilon_i \) is the eigenvalues of the Hamiltonian defined in the square bracket; \( \nu_i \) is given by

\[
\nu_i(r) = v(r) + \int dr' \frac{\rho(r')}{|r-r'|} + \frac{\delta E_{xc}[n]}{\delta \rho(r)} ,
\]

(1.30)

and

\[
D^l_{nm} = D^0_{nm} + \int dr \nu_i(r) Q^l_{nm}(r)
\]

(1.31)

The exchange correlation energy is given by \( E_{xc} = \int dr \rho(r) e_{xc}[\rho(r)] \).
Chapter 3: Electronic Structures and Magnetic Properties of Fe-Carbon Nanotube Systems

In this section the physics of carbon nanotubes (CN’s) is first reviewed. The details of calculations, the electronic structures, and the magnetic properties of the combined systems of Fe and carbon nanotubes of various sizes obtained from the *ab initio* molecular dynamics calculations are next discussed in detail. Finally, the curvature effects are investigated by comparing the electronic structures and magnetic properties of the combined system of graphite and Fe with those of the Fe-nanotube systems.

3.1 Physics of Carbon Nanotubes

A single single-wall carbon nanotube (SWCN) can be constructed by rolling up a single sheet of graphite (graphene) along one of its two-dimensional lattice vectors $R = na + mb$, to form an $(n,m)$ nanotube with diameter $D = |R|/\pi$. Neglecting the curvature, nanotubes are either semiconducting or metallic depending on whether or not $k_F \cdot R = 2p\pi$,\(^{29}\) where $p$ is an integer. In terms of $n$ and $m$, theoretical predictions\(^{30-32}\) imply that when the integer $|n-m|$ is (respectively, not) divisible by 3, the SWCN’s are metallic (respectively, semiconducting). The $(n,m)$ indices also determine the diameter of the
nanotube and the so-called “chirality.” \((m,m)\) tubes are “armchair” tubes, since the atoms around the circumference are in an armchair pattern (Fig. 3.1b). \((m,0)\) nanotubes are termed “zigzag” in view of the atomic configuration along the circumference (Fig. 3.1c). The other types of nanotubes are chiral, with rows of hexagons spiraling along the nanotube axes (Fig. 3.1d).
Fig. 3.1. A carbon nanotube can be constructed by rolling up a graphene sheet. Depending on the direction of rolling, the CN's are classified into three types: armchair (b), zigzag (c), and chiral (d) (from Image Gallery of R.E. Smalley).
3.2 Calculation Details

Following the *ab initio* molecular dynamics scheme,\textsuperscript{15} we optimize simultaneously the electronic wave function \( \{ \Psi_i \} \) and \( \{ \mathbf{R}_i \} \) by minimizing the total energy, using the CP codes.\textsuperscript{33} The Fe and carbon pseudopotentials constructed by Angelo are adopted.\textsuperscript{34} The Fe pseudopotential is devised to include the semicore 3s and 3p. In this way, the overlap of these states with the other valence states is accurately accounted for. Ultrasoft pseudopotentials are essentially as accurate as all-electron calculations, as shown for structural and vibrational properties of \( d \)-electron metals.\textsuperscript{36} The exchange-correlation energy is determined by using the Generalized Gradient Approximation.\textsuperscript{36,37}

All the calculations for the system of a pure carbon nanotube or a combined Fe-nanotube system are performed in an orthorhombic supercell with periodic boundary conditions (see Fig. 3.2). The spinor wave functions are expanded into a set of plane waves with cutoff energy of 25Ry. In the ultrasoft pseudopotential scheme, the cutoff energy of 250 Ry is used.

The geometry optimization is performed first for a pure CN. Fe atoms are then added, and the geometry optimization of the combined system is carried out. The total magnetic moment of the system is determined by allowing the spins to polarize in the process of optimization. The binding energy, Fermi energy, and band gap are also computed for various structures of Fe-CN systems. Depending on the initial structures, different structures corresponding to local minima are obtained. The structure corresponding to the global minimum is obtained by stretching the bonds of the structure having the lowest energy and then performing free molecular dynamics, followed by damped molecular
dynamics and quenching. The idea of this method is to shake the system out of the local minimum and allow it to go to the global minimum.

Fig. 3.2. Calculation model: CN in an orthorhombic supercell.
Three various carbon nanotubes of increasing diameter and decreasing curvature are considered here: CN(8,0), CN(12,0), and graphene.

3.3 Systems of a Carbon Nanotube (8,0) and Fe Atoms

The CN (8,0) is semiconducting and has a zigzag pattern (see also Section 3.1). For the pure nanotube, we obtain a gap of 0.49 eV and a diameter of 6.26 Å. The supercell contains a tube section of 64 C atoms and either one, two, three Fe atoms, or a chain of Fe atoms, and has dimensions in the x-, y-, and z-direction of 11.64, 11.64, 8.73 Å, respectively, which is sufficient for the interactions between the periodic images to become negligible. In the following sections, the electronic structures, band gap, Fermi energy, and magnetic properties for systems of CN(8,0) doped with one Fe atom, Fe clusters, and a chain of Fe atoms are presented.

3.2.1 Systems of a Carbon Nanotube (8,0) and One Fe Atom

Eight distinct sites (four inside and four outside the tube) of the Fe atom relative to the carbon nanotube surface are considered to investigate the interaction of a single Fe atom adsorbed on the (8,0) SWCN surface. Inside the tube four positions of Fe atom are labeled as follows: (i) hole position, IH (the Fe atom is above the center of a hexagon of six carbons), (ii) symmetric bond, IB1 (the Fe atom is above the center of the bond parallel to the axis of the tube), (iii) asymmetric bond, IB2 (the Fe atom is above the center of the bond along the radial direction of the tube), and (iv) top, IT (the Fe atom is right above a carbon atom). Similarly, corresponding to four structures of an Fe atom outside the tube, the abbreviations are OH (hole position outside the tube), OB1
(symmetric bond position outside the tube), OB2 (asymmetric bond position outside the tube), and OT (top position outside the tube). All sites are studied in such a way that the total energies are minimized, and all atoms are allowed to relax.

Figs. 3.3-3.4 show the optimized structures corresponding to these eight positions of the Fe atom inside and outside the tube. The results for these optimized structures are summarized in Tables 3.1-3.2. Table 3.1 lists the binding energy, the total magnetic moment $\mu$, and the charge transfer per Fe atom. The binding energy $E_b$ is a measure of the stability of a structure and is defined as the energy difference between the energy of the combined Fe-CN system and that of the pure CN and of the pure Fe atom:

$$E_b = E\,(\text{Fe-CN}) - E\,(\text{CN}) - E\,(\text{Fe})$$

The optimized bond lengths of the eight structures are given in Table 3.2. Six carbon atoms of the hexagon directly below/above the Fe atom are labeled from 1 to 6, as shown in Fig. 3.5.
Fig. 3.3. Four positions of the Fe atom inside the tube: IH (the Fe atom is above the center of a hexagon of six carbons), IB1 (the Fe atom is above the center of the C-C bond parallel to the axis of the tube), IB2 (the Fe atom is above the center of the C-C bond along the radial direction of the tube), and IT (the Fe atom is right above a carbon atom).
Fig. 3.4. Four positions of the Fe atom outside the tube: OH (the Fe atom is above the center of a hexagon of six carbons), OB1 (the Fe atom is above the center of the C-C bond parallel to the axis of the tube), OB2 (the Fe atom is above the center of the C-C bond along the radial direction of the tube), and OT (the Fe atom is right above of a carbon atom).
Table 3.1. Binding energy (in eV), total magnetic moment $\mu_M$ (in Bohr magneton, $\mu_B$), and charge transfer per Fe atom, for all optimized structures.

<table>
<thead>
<tr>
<th>Position</th>
<th>$E_b$ (eV)</th>
<th>$\mu_M$ ($\mu_B$)</th>
<th>Charge transfer (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inside</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hole (IH)</td>
<td>Present</td>
<td>-1.079</td>
<td>2.00</td>
</tr>
<tr>
<td></td>
<td>Ref. 39</td>
<td>-1.070</td>
<td>2.36</td>
</tr>
<tr>
<td>Top (IT)</td>
<td>Present</td>
<td>-1.124</td>
<td>4.00</td>
</tr>
<tr>
<td></td>
<td>Ref. 39</td>
<td>-0.800</td>
<td>2.44</td>
</tr>
<tr>
<td>Bond1 (IB1)</td>
<td>Present</td>
<td>-0.919</td>
<td>4.00</td>
</tr>
<tr>
<td></td>
<td>Ref. 39</td>
<td>-1.150</td>
<td>2.22</td>
</tr>
<tr>
<td>Bond2 (IB2)</td>
<td>Present</td>
<td>-1.121</td>
<td>4.00</td>
</tr>
<tr>
<td><strong>Outside</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hole (OH)</td>
<td>Present</td>
<td>-1.413</td>
<td>2.00</td>
</tr>
<tr>
<td></td>
<td>Ref. 39</td>
<td>-1.400</td>
<td>3.90</td>
</tr>
<tr>
<td>Top (OT)</td>
<td>Present</td>
<td>-0.941</td>
<td>4.00</td>
</tr>
<tr>
<td></td>
<td>Ref. 39</td>
<td>-0.650</td>
<td>3.93</td>
</tr>
<tr>
<td>Bond1 (OB1)</td>
<td>Present</td>
<td>-1.057</td>
<td>4.00</td>
</tr>
<tr>
<td></td>
<td>Ref. 39</td>
<td>-0.850</td>
<td>3.92</td>
</tr>
<tr>
<td>Bond2 (OB2)</td>
<td>Present</td>
<td>-0.954</td>
<td>4.00</td>
</tr>
</tbody>
</table>
Fig. 3.5. Six carbon atoms of the hexagon directly below/above the Fe atom.

Table 3.2. Optimized bond length values of the eight structures. Bond length is in Å.

The six carbon atoms of the hexagon are labeled from 1 to 6, as shown in Fig. 3.5.

<table>
<thead>
<tr>
<th></th>
<th>Fe-C₁</th>
<th>Fe-C₄</th>
<th>Fe-C₂</th>
<th>Fe-C₃</th>
<th>Fe-C₅</th>
<th>Fe-C₆</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inside</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bond1 (IB1)</td>
<td>Present</td>
<td>2.08</td>
<td>2.09</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bond1 (IB1)</td>
<td>Ref. 39</td>
<td>2.00</td>
<td>2.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bond2 (IB2)</td>
<td>Present</td>
<td>2.02</td>
<td>2.09</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hole (IH)</td>
<td>Present</td>
<td>2.18</td>
<td>2.17</td>
<td>2.04</td>
<td>2.04</td>
<td>2.05</td>
</tr>
<tr>
<td>Hole (IH)</td>
<td>Ref. 39</td>
<td>2.20</td>
<td>2.20</td>
<td>2.10</td>
<td>2.10</td>
<td>2.10</td>
</tr>
<tr>
<td>Top (IT)</td>
<td>Present</td>
<td>2.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Outside</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bond1 (OB1)</td>
<td>Present</td>
<td></td>
<td>2.07</td>
<td>2.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bond1 (OB1)</td>
<td>Ref. 39</td>
<td></td>
<td>2.10</td>
<td>2.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bond2 (OB2)</td>
<td>Present</td>
<td>2.08</td>
<td>2.13</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hole (OH)</td>
<td>Present</td>
<td>2.06</td>
<td>2.06</td>
<td>2.19</td>
<td>2.20</td>
<td>2.19</td>
</tr>
<tr>
<td>Hole (OH)</td>
<td>Ref. 39</td>
<td>2.10</td>
<td>2.10</td>
<td>2.40</td>
<td>2.40</td>
<td>2.40</td>
</tr>
<tr>
<td>Top (OT)</td>
<td>Present</td>
<td>1.99</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
As seen from Table 3.1, for the case of the Fe atom inside the tube the two most stable structures are the IT and IB2, with binding energies of -1.124 eV and -1.121 eV, respectively; this is in contrast to Ref. 38, where it is found that the most stable structure was IB1 (in Ref. 38 the geometry similar to IB2 is not considered). For the case of the Fe atom outside the tube, however, the most stable structure is the OH of binding energy of -1.413 eV, consistent with the finding of Fagan et al. 38 The discrepancy between the results of Ref. 38 and ours may arise from the fact that in the former calculation, a norm-conserving pseudopotential with a low cutoff energy (150 Ry) is used. In the present work, however, the ultrasoft pseudopotential with a higher energy cutoff (250 Ry) is used. The ultrasoft pseudopotential is known to provide a better treatment of $d$-electron metals than does the norm-conserving pseudopotential since it allows for the inclusion of semicore $3s$ and $3p$. Furthermore, the higher the cutoff energy, the more accurate the results, because higher cutoff energy implies a larger basis set being used. Comparison of the binding energy for the cases of Fe inside and outside the tube reveals that the OH configuration is the most stable structure. This does not mean that, however, CN’s cannot be filled with Fe. Since the difference in binding energy of the configurations corresponding to the Fe atom inside and outside the tube is small (-0.3eV), filling carbon nanotubes with Fe atoms is possible. This result is consistent with the experimental studies showing Fe clusters inside 39 and outside 8 CN’s.

The total magnetic moments $\mu$ for the Fe-SWCN achieve nonzero finite values. For most of the structures listed in Table 3.1 the total magnetic moments $\mu_M$ are 4.00 $\mu_B$, except for the IH and OH configurations, for which the total magnetic moments are 2.00 $\mu_B$. These results contrast with those Ref. 38, where it was found that the values of $\mu_M$ is
about 2.2 to 2.4 $\mu_B$ for all the positions of the Fe atoms inside the tube, and $\sim 3.9 \mu_B$ for all positions of the Fe atoms outside the tube. Since the total magnetic moment of a single Fe atom in vacuum is 4.0 $\mu_B$, it is interesting to point out that a reduction of the total magnetic moment of the Fe atom occurs only when it is at the hole position.

For all configurations considered, there is a charge transfer from the Fe atom to the CN. Since there is a partial charge transferred from the Fe atom to the CN, bonding between the Fe and C atoms is not purely covalent or ionic but has both covalent and ionic characters. For the case of an Fe atom inside a carbon nanotube, the amount of charge transfer is found to be higher for the cases of IT and IB2 than for the cases of IH and IB1 (see Table 1). This implies that the bonding between the Fe and C atoms has more ionic character when the Fe atom is at the top and at the asymmetric bond positions than when the Fe atom is at the hole and at the symmetric bond positions. On the other hand, for the case outside the tube, the Fe-C bond has more ionic character when the Fe atom is at the hole position than when the Fe atom is at other positions. Moreover, since more charge is transferred from the Fe atom to the CN for the case inside the tube than for the case outside the tube, the bonding between an Fe atom inside the tube with the CN surface has more ionic character than that outside the tube.

It is interesting to point out that the difference in the most stable structures between the tube-inside and tube-outside cases clearly results from the difference in curvature. The curvature effect can also be observed in the variation of the bond length for different locations of the Fe relative to the tube surface. As seen from Table 3.2, while the difference in bond length for the cases IB1 and OB1 is small, there is a distinct difference in the bond lengths for the cases of IH and OH (see Fig. 3.6). For the IH configuration,
the Fe-C\textsubscript{1} and Fe-C\textsubscript{4} bonds are (~2.18 Å) longer than Fe-C\textsubscript{2}, Fe-C\textsubscript{3}, Fe-C\textsubscript{5}, and Fe-C\textsubscript{6} bonds (~2.04 Å). On the other hand, for the structure OH, the opposite situation is observed: the Fe-C\textsubscript{1} and Fe-C\textsubscript{4} bonds are shorter than Fe-C\textsubscript{2}, Fe-C\textsubscript{3}, Fe-C\textsubscript{5}, and Fe-C\textsubscript{6}.

Fig. 3.6. Difference in bond length of structures IH and OH is a consequence of the curvature effect. The Fe-C bond length along C\textsubscript{1}-C\textsubscript{4} is shorter for the OH than for the IH configurations. The opposite behavior occurs for the Fe-C bond length along C\textsubscript{2}-C\textsubscript{5} and C\textsubscript{3}-C\textsubscript{6}. 
The effect of curvature and hybridization between the Fe atom and the tube can be seen in Figs. 3.7-3.8, where the electron density distributions are plotted in the cut-planes passing through the carbon atoms C₁-Fe-C₄ and C₂-Fe-C₅ for the IH and OH configurations, respectively. There is a clear covalent character in the interaction between the Fe atom and the SWCN, for the inside as well as for the outside configurations. As seen from Fig. 3.7, for the IH configuration, the interaction between the Fe atom and the atoms C₂ and C₅ (similarly for C₃ and C₆) is stronger than that between the Fe atom and C₁ and C₄, as indicated by a larger degree of overlapping of the corresponding electron density distributions of the Fe atom and the atoms C₂ and C₅ than that of the Fe atom and the atoms C₁ and C₄. As a result, the length of the bonds Fe-C₂ and Fe-C₅ is shorter than that of the bonds Fe-C₁ and Fe-C₄. For the OH configuration, on the other hand, an opposite behavior is observed: The interaction between the Fe atom with the atoms C₂ and C₅ is weaker than that of the Fe atom with C₁ and C₄. Consequently, the length of the bonds Fe-C₂ and Fe-C₅ is longer than that of the bonds Fe-C₁ and Fe-C₄. The large values of the binding energies (Table 3.1) come from the covalently bonding between the Fe and carbon atoms.

As discussed in the previous paragraph, the bonding between Fe and C atoms has both ionic and covalent nature. This raises the question: Does the interaction between the Fe atom and SWCN cause any change in electronic properties of the CN such as band gap and Fermi energy? The analysis of our results shows that the answer is yes. Table 3.3 summarizes the Fermi energy and band gap values of the combined Fe-SWCN system as well as those of the pure SWCN. In Table 3.3, $E_F$ and $E_g$ are the Fermi energy and band gap, respectively. Comparison between the Fe-SWCN system and the pure SWCN is
made by computing the difference in Fermi energy and band gap $\Delta E_F$ and $\Delta E_g$ (Table 3.3).

Table 3.3. Fermi Energy and band gap of the pure SWCN and the Fe-SWCN system. $E_F$ (in eV) and $E_g$ (in eV) are the Fermi energy and band gap, respectively. $\Delta E_F$ and $\Delta E_g$ are differences in Fermi energy and band gap between the Fe-SWCN system and the pure SWCN, respectively.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>$E_F$ (eV)</th>
<th>$E_g$ (eV)</th>
<th>$\Delta E_g$ (eV)</th>
<th>$\Delta E_F$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure SWCN</td>
<td>-1.681</td>
<td>0.490</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-SWCN</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IH</td>
<td>-1.465</td>
<td>0.216</td>
<td>0.273</td>
<td>0.216</td>
</tr>
<tr>
<td>IB1</td>
<td>-1.415</td>
<td>0.245</td>
<td>0.245</td>
<td>0.266</td>
</tr>
<tr>
<td>IB2</td>
<td>-1.468</td>
<td>0.400</td>
<td>0.090</td>
<td>0.213</td>
</tr>
<tr>
<td>IT</td>
<td>-1.474</td>
<td>0.402</td>
<td>0.088</td>
<td>0.207</td>
</tr>
<tr>
<td>OH</td>
<td>-1.354</td>
<td>0.320</td>
<td>0.170</td>
<td>0.327</td>
</tr>
<tr>
<td>OB1</td>
<td>-1.423</td>
<td>0.219</td>
<td>0.271</td>
<td>0.258</td>
</tr>
<tr>
<td>OB2</td>
<td>-1.418</td>
<td>0.089</td>
<td>0.401</td>
<td>0.263</td>
</tr>
<tr>
<td>OT</td>
<td>-1.433</td>
<td>0.225</td>
<td>0.265</td>
<td>0.248</td>
</tr>
</tbody>
</table>
Fig. 3.7. Electron density distribution for IH configuration plotted in the cut-planes passing through the atoms a) C₁-Fe-C₄ and b) C₂-Fe-C₅.

Fig. 3.8. Electron density distribution for OH configuration plotted in the cut-planes passing through atoms a) C₁-Fe-C₄ and b) C₂-Fe-C₅.
As seen from Table 3.3, the Fermi energy of the Fe-SWCN system increases, and the band gap decreases, compared to that of the pure CN. An increase in Fermi energy and a decrease in band gap can be attributed partially to the charge transfer from the Fe atom to the CN, even though it is not the only reason to cause this change. Other reasons may include the back charge transfer from the CN to the Fe atom, and spin splitting. Furthermore, the variation in band gap $E_g$ depends on each configuration. The change in band gap is smallest for the cases of IB2 and IT. It is interesting to point out that the decrease in the band gap for the case of OB2 is so significant that the combined system Fe-CN becomes semimetallic (very small band gap $E_g = 0.089$eV), while for other cases the Fe-CN systems still behave as semiconductors.

3.2.2 Systems of a Carbon Nanotube (8,0) and Clusters of Fe Atoms

Similar to the case of one Fe atom inside a SWCN, clusters of Fe atoms inside a SWCN are also studied. Figs. 3.9 and 3.10 show the optimized configurations of a dimer Fe$_2$ and a trimer Fe$_3$ inside a SWCN. Table 3.4 lists the binding energy, total magnetic moments, and the Fe-Fe and Fe-C bond lengths inside the CN. Since the binding energies and total magnetic moments depend on the initial structures, many local minima are obtained for various configurations. In Table 3.4, only one local minimum and the global minimum are given for Fe$_2$ and Fe$_3$ clusters inside the tube. The binding energies of the most stable structures of the dimer Fe$_2$ and trimer Fe$_3$ clusters are -3.66 eV and -7.15 eV, respectively. The total magnetic moments are 6.0 $\mu_B$ and 2.0 $\mu_B$. However, the total magnetic moment for the most stable structure of a dimer Fe$_2$ in vacuum is 12.00 $\mu_B$, and 8.00 $\mu_B$ for the most stable structure of trimer Fe$_3$ in vacuum (see Table 3.5).
Clearly, the total magnetic moments of the dimer Fe$_2$ and trimer Fe$_3$ inside a SWCN are reduced compared to those in the vacuum. This reduction results from bond formation, in which a spin-pairing process between the Fe and C atoms has removed part of the spins from each Fe atom (see also Figs. 3.9 and 3.10).

It is noted that while the binding energy between an Fe atom with SWCN is less than -1.5 eV (see Table 3.1), the binding energy of Fe-Fe is -2.43 eV; that is, the Fe-Fe bond is stronger than the Fe-CN bond. Therefore, it is expected that Fe atoms inside/outside the SWCN will tend to form clusters, as observed in the experiments of Dai et al. Fig. 3.11 shows the nanowires of various metals prepared on carbon nanotube templates. Depending on the difference between the metal-metal interaction and the metal-tube interaction, continuous or discontinuous nanowires can be formed. For example, while for Ti a continuous wire is formed, for Fe only discontinuous clusters are formed.
Table 3.4. Binding energy, total magnetic moment, and Fe-Fe bond length \( D_{(\text{Fe-Fe})} \) (in Å).

The global minimum corresponds to the configuration having the lowest binding energy for clusters of two and three Fe atoms inside the tube.

<table>
<thead>
<tr>
<th>Fe Cluster-CN</th>
<th>( E_b ) (eV)</th>
<th>( \mu_M ) (( \mu_B ))</th>
<th>( D_{(\text{Fe-Fe})} ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2Fe-CN</td>
<td>-3.66</td>
<td>6.00</td>
<td>2.298</td>
</tr>
<tr>
<td></td>
<td>-2.95</td>
<td>0</td>
<td>2.223</td>
</tr>
<tr>
<td>3Fe-CN</td>
<td>-7.15</td>
<td>2.00</td>
<td>2.25, 2.25, 2.43</td>
</tr>
<tr>
<td></td>
<td>-6.98</td>
<td>0</td>
<td>2.36, 2.36, 2.42</td>
</tr>
</tbody>
</table>

Table 3.5. Binding energy, total magnetic moment, and Fe-Fe bond length \( D_{(\text{Fe-Fe})} \) (in Å) of clusters of Fe (Fe\(_2\) and Fe\(_3\)) in vacuum.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>( E_b ) (eV)</th>
<th>( \mu_M ) (( \mu_B ))</th>
<th>( D_{(\text{Fe-Fe})} ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(_2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-2.43</td>
<td>8.00</td>
<td>2.00</td>
</tr>
<tr>
<td>Fe(_3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-5.109</td>
<td>12.00</td>
<td>2.30, 2.30, 2.30</td>
</tr>
<tr>
<td></td>
<td>-5.092</td>
<td>10.00</td>
<td>2.29, 2.12, 2.30</td>
</tr>
<tr>
<td></td>
<td>-4.655</td>
<td>8.00</td>
<td>2.17, 2.17, 2.16</td>
</tr>
<tr>
<td></td>
<td>-4.366</td>
<td>4.05</td>
<td>2.12, 2.42, 2.42</td>
</tr>
</tbody>
</table>
Fig. 3.9. Optimized structures of 2Fe-CN systems: multiplicity $2S+1 = 7$ (a), $2S+1 = 1$ (b), where $S$ is total spin.

Fig. 3.10. Optimized structures of 3Fe-CN systems: multiplicity $2S+1 = 3$ (a), $2S+1 = 1$ (b).
Fig. 3.11. Various metallic nanowires prepared on carbon nanotube templates (from Ref. 8). From top to bottom, the metals are: Ti (a), Ni (a), Pd (c), Fe (d), Au (e), Al (f). While for Ti a continuous wire is formed, for Fe only discontinuous clusters are formed. Note that the sizes of these nanowires are much larger (nanometer scale) than the Fe-CN systems considered here, where very small clusters of a few Fe atoms (less than 7 Å) lie inside a SWCN of small diameter (6.26 Å).
3.2.3 Systems of a Carbon Nanotube (8,0) and a Chain of Fe Atoms

Several chain configurations and their relative positions relative to the carbon surface are considered. Shown in Table 3.6 are two configurations, one with the very high-stoichiometry packing of Fe₄C₃₂ (chain 1) and the other (chain 2), with the stoichiometric formula of Fe₅C₃₂ (see Figs. 3.12-3.13). In the former case, the calculation is performed in a supercell containing a section of 32C and 4 Fe atoms, with periodic boundary conditions. For the latter case, the supercell has 64C and 6 Fe atoms. In contrast to the case of a single Fe atom inside the tube, it is hard to determine whether the position of each Fe atom in the chain is the hole, top, or bond position. Table 3.6 lists the corresponding binding energies and the total magnetic moments for these two configurations. The minimum and maximum Fe-Fe distances \( D_{(Fe-Fe)} \) and the Fe-C distances, \( D_{(Fe-C)} \), are also given. Both chains have zigzag configurations. For the case of chain 1, because of the high packing, the tube deforms (Fig. 3.12). The binding energies are -4.10 eV per Fe atom and -2.86 eV per Fe atom for chain 1 and chain 2, respectively. The total magnetic moment for the chain 2 (3.0\( \mu_B \)/atom) is much larger than that for chain 1 (1.0\( \mu_B \)/atom). This difference is due to the fact that more electrons of Fe atoms in chain 1 participate in forming the bond with CN, as indicated by Fe-C bonds for the case of chain 1 being shorter than those for the case of chain 2. The band gap energy is 0.43 eV for the case of chain 1, and 0.39 eV for the case chain 2, respectively. The SWCN’s still behave as semiconductors in these cases.

In order to compare the total magnetic moments of a chain inside a CN and that in vacuum, the same initial chain configuration of chain 2 (zigzag configuration) is used as initial structure input for optimization of a zigzag chain in vacuum. As expected, the
zigzag chain clumps into a cluster after optimization. The corresponding binding energy and total magnetic moment obtained for this configuration are -2.53 eV per Fe atom and 2.33 $\mu_B$ Fe atom per atom, respectively. Clearly, due to the confinement of the tube, the chain in the tube cannot form a cluster but maintains a zigzag configuration. As a result, the chain in the tube has a larger total magnetic moment. This result is very plausible, since ideal one-dimensional magnetic nanowires with enhanced magnetic moment can be made by using a small diameter SWCN.

Table 3.6. Binding energies, total magnetic moments, and bond length of Fe chains inside a carbon nanotube.

<table>
<thead>
<tr>
<th>Fe Chain-CN</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stoichiometry</td>
<td>Fe$<em>4$C$</em>{32}$</td>
<td>Fe$<em>6$C$</em>{64}$</td>
</tr>
<tr>
<td>$E_b$ (eV)/Fe atom</td>
<td>-4.10</td>
<td>-2.86</td>
</tr>
<tr>
<td>$\mu_M(\mu_B)/$atom</td>
<td>1.00</td>
<td>3.00</td>
</tr>
<tr>
<td>$E_g$ (eV)</td>
<td>0.43</td>
<td>0.39</td>
</tr>
<tr>
<td>$D_{(Fe-Fe)}$</td>
<td>2.38-2.61</td>
<td>2.29-2.52</td>
</tr>
<tr>
<td>$D_{(Fe-C)}$</td>
<td>2.06, 2.06, 2.08, 2.12</td>
<td>2.12, 2.24, 2.14, 2.13, 2.18, 2.18</td>
</tr>
</tbody>
</table>
Fig. 3.12. A chain inside a SWCN with high stochiometric packing Fe$_4$C$_{32}$: side view (a) and top view (b).

Fig. 3.13. A chain inside a SWCN with stoichiometric packing Fe$_6$C$_{32}$: side view (a) and top view (b).
3.4 Systems of a Carbon Nanotube (12,0) and One Fe Atoms

In order to investigate curvature (and size) effects the interaction of an iron atom with a SWCN, a system of one Fe inside a SWCN of larger diameter (12,0) is also studied. CN (12,0) is a zigzag and semimetallic nanotube with a diameter of 9.40 Å. All calculations are performed in a supercell having 96C and dimensions of 14.82x14.82x8.44 Å with periodic boundary conditions. Similar to the case of one Fe atom inside the CN(8,0), four different sites of the Fe atom are considered: hole (IH), top (IT), bond1 (IB1), and bond2 (IB2). The binding energies, total magnetic moments, and bond length for the optimized configurations are summarized in Table 3.7. In contrast to the case of the small diameter tube CN(8,0), the most stable configuration is IH. Similar to the case of CN(8,0), compared to the total magnetic moment of a single Fe atom in vacuum, a reduction of total magnetic moment occurs when the Fe atom is at the hole position (IH).

Table 3.7. Binding energy, total magnetic moments, and bond length. Carbons C₁ to C₆ are labeled as in Fig. 3.5.

<table>
<thead>
<tr>
<th>Position</th>
<th>$E_b$ (eV)</th>
<th>$\mu_M$ (μB)</th>
<th>Bond length</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Fe-C₁</td>
</tr>
<tr>
<td>Bond1</td>
<td>-0.837</td>
<td>4</td>
<td>2.28</td>
</tr>
<tr>
<td>Bond2</td>
<td>-0.900</td>
<td>4</td>
<td>2.14</td>
</tr>
<tr>
<td>Hole</td>
<td>-1.445</td>
<td>2</td>
<td>2.13</td>
</tr>
<tr>
<td>Top</td>
<td>-0.872</td>
<td>4</td>
<td>2.13</td>
</tr>
</tbody>
</table>
3.5 Systems of a Graphene Sheet and Adsorbed Fe Atoms

A sheet of graphite (graphene) corresponds to the extreme case of a carbon nanotube of infinite diameter (zero curvature). The interaction of an iron atom with graphene is also investigated for the three different positions of the Fe atom: hole (HG), bond (BG), and top (TG) positions. Fig. 3.14 shows optimized structures corresponding to these positions of the Fe atom. The binding energy, total magnetic moment, and charge transfer are given in Table 3.8. The most stable configuration is the one with the Fe atom at the hole position, which is similar to the case of the large tube CN(12,0). The binding energies and the amount of charge transfer for the case of Fe-graphene however are smaller than for the two previous cases of Fe-CN(8,0) and Fe-CN(12,0). Clearly, the presence of curvature in the CN leads to a stronger bonding between the Fe atoms with SWCN than with graphene.

For the HG configuration, the present binding energy is about half that from the study of Duffy et al.\textsuperscript{40} The discrepancy results from the different methods used in determining the exchange-correlation energy. While in Ref. 40, the LDA is used, in this study the GGA, which is known to give more accurate estimates of the exchange-correlation energy, is used.
Fig. 3.14. Optimized geometries of an Fe atom adsorbed on a graphene sheet: a) Fe atom at hole position, b) Fe atom at bond position, c) the Fe atom at top position.
Table 3.8. Binding energy, total magnetic moment, and charge transfer. \( z \) (in \( \text{Å} \)) is the average distance from the Fe atom to the surface of graphite. \( D_{\text{C-Fe}} \) (in \( \text{Å} \)) is the C-Fe bond length.

<table>
<thead>
<tr>
<th>Position</th>
<th>( E_h ) (( \text{Å} ))</th>
<th>( \mu_m (\mu_B) )</th>
<th>Charge transfer</th>
<th>( z ) (( \text{Å} ))</th>
<th>( D_{\text{C-Fe}} ) (( \text{Å} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hole</td>
<td>Present</td>
<td>-1.084</td>
<td>2</td>
<td>0.3499</td>
<td>1.49</td>
</tr>
<tr>
<td>Hole</td>
<td>Ref. 40</td>
<td>-2.000</td>
<td>2</td>
<td>-</td>
<td>1.52</td>
</tr>
<tr>
<td>Bond</td>
<td></td>
<td>-0.273</td>
<td>4</td>
<td>0.1619</td>
<td>2.30</td>
</tr>
<tr>
<td>Top</td>
<td></td>
<td>-0.376</td>
<td>4</td>
<td>0.1645</td>
<td>2.06</td>
</tr>
</tbody>
</table>
3.6 Curvature Effects

The effects of curvature on the interaction of the Fe atoms with SWCN’s and graphene are summarized Fig. 3.15. For the case of Fe inside the tube, the most stable structure changes from the bond/top for CN(8,0) to the hole position for CN(12,0) and graphene. In other words, as the tube curvature changes, the most stable structure varies, and the most stable configuration is the hole position. Furthermore, the most stable structure for the case of Fe outside the small tube is also the hole position. This similarity indicates that curvature effects are most pronounced for the small diameter carbon nanotubes, in accord with intuition.

<table>
<thead>
<tr>
<th>System</th>
<th>Fe-CN(8,0)</th>
<th>Fe-CN(12,0)</th>
<th>Graphene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (Å)</td>
<td>6.3</td>
<td>9.3</td>
<td>∞</td>
</tr>
<tr>
<td>Inside tube</td>
<td>Bond/Top</td>
<td>Hole</td>
<td>Hole</td>
</tr>
<tr>
<td>Outside tube</td>
<td>Hole</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3.15. Effects of curvature: the most stable structure changes as the curvature varies.
3.7 Suggestions for Future Work

In this thesis, the magnetic exchange interactions between Fe atoms inside the tube as well as between Fe atoms inside adjacent tubes have not been studied, because the errors of the current method are too large to allow for accurate determinations of these interactions. In future research, more accurate pseudopotentials must be developed, which will allow more accurate determination of magnetic couplings. Since different metals will interact differently with carbon nanotubes, especially magnetic rare-earth metals such as Gd, where relativistic effects have to be taken into account, it would also be of interest to study the interaction of Gd with carbon nanotubes.
Part II

Magnetic Phase Transitions and Long-Range Order of Magnetic Carbon Nanotubes
Chapter 4: Introduction

This part extends and complements Part I by approximating the magnetic interactions between the magnetic ions filling the CN's and between the magnetic ions of adjacent CN's, and by using statistical mechanics to investigate the resulting phase diagram of the corresponding Hamiltonian.

As described in Chapter I, the discovery of carbon nanotubes (CN) and the theoretical predictions of their remarkable electronic properties have stimulated much interest at the fundamental and technological levels.\textsuperscript{1-4} Similar to intercalation graphite compounds, carbon nanotubes can be intercalated with other elements. Filling of foreign elements or compounds into carbon nanotubes by the wetting method has been studied experimentally.\textsuperscript{5-13} The filling materials range from ionic compounds (e.g., KI, KBr), nonmetallic elements (e.g., I\textsubscript{2}, Si), to metallic elements (e.g., K, Au). On the other hand, previous theories predict\textsuperscript{14} that small carbon nanotubes can be filled with a single chain of metal atoms by the gas phase method. This is confirmed by the recent work of Hirahasa et al.,\textsuperscript{15} who describe intercalation of the magnetic rare-earth metal Gd in the form of metallofullerene Gd@C\textsubscript{82} inside carbon nanotubes.

There is increasing interest in carbon nanotubes filled with magnetic transition metals\textsuperscript{16-18} (Fe, Co, and Ni) because of their potential applications in making recording
materials, in which carbon nanotubes serve to protect the transition metals against air-oxidation. Furthermore, magnetic hysteresis curves are observed experimentally for the cases of Fe- and Co-filled carbon nanotubes.\textsuperscript{17} Noteworthy among these studies is that of R. S. Iskhakov \textit{et al.},\textsuperscript{18} who experimentally showed that ferromagnetic Fe particles in carbon nanotubes are exchange-coupled, as indicated by the cooperative phenomena revealed in the field and temperature dependence of the magnetization in a system of iron nanoparticles in carbon nanotubes.

Although controlled intercalation of magnetic transition metals into carbon nanotubes at the atomic level (e.g., a single chain of atoms inside a carbon nanotube) has not yet been realized experimentally, intercalating graphite with magnetic transition metals and rare-earth metals has been extensively studied theoretically and experimentally.\textsuperscript{19-23} These studies have showed that magnetic transition and rare-earth atoms are coupled across several parallel graphene sheets. In addition, studies of fullerenes compounds, which are closer to carbon nanotubes than graphite, also indicate that metallofullerenes (fullerenes endohedrally doped with transition- and rare-earth metals) are successfully synthesized.\textsuperscript{24} In particular, depending on the nature of metals, ferromagnetic or antiferromagnetic couplings have been observed between endohedral metallofullerene molecules M@C\textsubscript{82} (where M is a rare-earth atom) at low temperature.\textsuperscript{25} These studies have clearly established that such a magnetic coupling does not vanish across two graphene sheets and possibly more, and therefore that three-dimensional long-range magnetic order is possible (see Ref. 7 of Part I).

It is this possibility that we investigate theoretically in the present work for the case of arrays of carbon nanotubes filled with magnetic ions, observing that the coupling
between two magnetic ions in neighboring nanotubes is similar to that between two magnetic ions separated by graphene sheets in magnetic transition-metal intercalated graphite compounds or in endohedral metallofullerenes.

In Part I of this thesis, we showed that filling carbon nanotubes with Fe is energetically favorable, and the carbon nanotubes become magnetized. In the present Part II, we investigate the thermodynamic properties of networks of magnetic SWCN’s, with emphasis on long range magnetic order and on the phase transition from the nonmagnetic (paramagnetic) phase to the magnetic (ferromagnetic) phase.
Chapter 5: Elements of Magnetism

Magnetism phenomena have been known and used for several centuries. No theory could explain these natural phenomena until the advent of quantum mechanics. This chapter gives a brief description of magnetic properties of a paramagnet, a system of non-interacting magnetic atoms, and of a ferromagnet, a system containing interacting magnetic atoms.

Magnetic properties of a material are classified by its response to an applied magnetic field. This response is characterized by the susceptibility, $\chi$, in the relation:

$$M = \chi H_o,$$

where $M$ is the magnetization, or magnetic moment per unit volume, and $H_o$ is the applied field. In general, $\chi$ is a function of both $H_o$ and temperature $T$. If the material is magnetically isotropic, $M$ and $H_o$ are parallel, and $\chi$ is a scalar; for anisotropic materials, $\chi$ is a tensor.

Diamagnetic materials are those that expel an applied magnetic field and have a small negative temperature-independent susceptibility. In diamagnetic materials, all electrons are paired according to the Pauli exclusion principle. Under an external magnetic field, a magnetic field is induced in an opposite direction to the magnetic field. This type of
magnetism is a direct consequence of Lenz's law applied to the motion of the elementary charges (generally electrons) of the system. All materials have diamagnetic contributions to their susceptibilities.

Paramagnetic materials are those that are attracted by an applied magnetic field and have a positive temperature-dependent susceptibility. The phenomenon of paramagnetism occurs only in materials in which individual atoms or molecules have permanent magnetic moments which result from unpaired electrons. This kind of magnetic behavior can be explained as a consequence of two opposing effects: one, the tendency of the applied field to orient the moments in the direction of the field, and the other, the tendency of thermal agitation to preserve a random orientation of magnetic moments. The paramagnetic susceptibility varies linearly with $H_o$ for small fields and consequently vanishes for zero applied field.

However, it is also well known that some crystals containing magnetic atoms develop a macroscopic magnetic moment in the absence of an applied field if they are cooled to sufficiently low temperatures. This self-magnetization, or spontaneous magnetization, is a result of the interaction between magnetic atoms which tend to align their magnetic moments. A spontaneously magnetized crystal is an example of a cooperative system, in which the constituents interact so strongly that they cannot, in any reasonable approximation, be considered independent of each other. Such substances can be classified into four classes: ferromagnetic, antiferromagnetic, ferrimagnetic, and helimagnetic.

In a ferromagnetic material (e.g., Fe, Co, Ni, Gd), the interactions between the magnetic atoms favor a parallel alignment of the atomic magnetic moments. At absolute
zero, the alignment is complete, and the spontaneous magnetization decreases with increasing temperature, gradually at first, and then more and more rapidly, until it becomes zero at a characteristic temperature known as the Curie temperature.

5.1 Magnetic Moments

Each individual electron in an atom has an angular momentum associated with its orbital motion, plus an intrinsic, or spin, angular momentum. For an n-electron atom, these 2n angular momenta then couple together to give a total angular momentum whose exact properties depend on the details of the coupling parameters. For most atoms and ions, the angular momentum states can be described by the Russell-Saunders model of atomic structure. In the Russell-Saunders scheme, the individual orbital angular momenta couple together to give a total orbital angular momentum \( L \), and the individual spin angular momenta couple together to give a total spin angular momentum \( S \). Finally, \( L \) and \( S \) couple to give a total angular momentum \( J \). The orbital angular momentum state of an atom is characterized by the eigenvalues of \( L^2 \) and one of the components of \( L \), generally chosen to be \( L_z \); similar results hold for the spin and the total angular momentum states.

The orbital and spin angular momenta each have a magnetic moment associated with them, the magnetic moment operators being given by\(^{26}\)

\[
\mu_L = -\frac{|e| \hbar}{2m_e c} L = -\mu_B L \\
\mu_S = -2\mu_B S, 
\]  

(5.2)
where the quantity $\mu_\beta = e|\hbar/(2m_e c)$ is a unit of magnetic moment equal to $0.927 \times 10^{-20}$ erg/oersted; it is generally called the Bohr magneton.

The total magnetic moment is defined as

$$\mu = -\mu_\beta (L + 2S) \quad (5.3)$$

The vector diagram in Fig. 5.1 shows how $L$ and $S$ combine to give a total magnetic moment $\mu$. In the absence of an applied field, the total angular momentum $J$ is a constant of the motion; $L$, $S$, and $\mu$, on the other hand, are constant in magnitude but precess about $J$, so that the component of $\mu$ perpendicular to $J$ averages to zero when taken over a time that is large compared with the precession period. Thus, an applied magnetic field can sense only the component of $\mu$ parallel to $J$, which is called here $\mu_J$. The eigenvalues of the total magnetic moment and its $z$-components are given by

$$\mu_J^2 = g^2 J(J+1)\mu_\beta$$

$$\mu_J = -g \mu_y J_z \quad (5.4)$$

where $g$, the Lande $g$-factor or spectroscopic splitting factor, is given by

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad (5.5)$$
Fig. 5.1. Vector relation between the spin, orbital, and total angular momenta and associated magnetic moments (from Ref. 26)

### 5.2 Paramagnetism

Consider a system of $N$ identical magnetic atoms with total angular momentum $J$ and magnetic moment $\mu_r$. As the atoms do not interact with each other, the only contributions to the Hamiltonian come from their interaction with the applied magnetic field, and as they are identical, only the Hamiltonian for a single atom is considered:

$$\mathcal{H} = - \mu_r \cdot H_0.$$  \hspace{1cm} (5.6)

Without loss of generality $H_0$ can be chosen to be along the $z$-axis:

$$\mathcal{H} = - \mu_r \cdot H_0.$$  \hspace{1cm} (5.7)

The partition function is

$$Z_J = \sum_{m = -J}^{J} \exp\left(- g\mu_B JH_0 / kT\right).$$  \hspace{1cm} (5.8)

It is convenient to express $Z_J$ in the form

$$Z_J(x) = \sum_{m = -J}^{J} e^{mxJ} = \frac{\sinh\left(\frac{2J + 1}{J} x\right)}{\sinh\left(\frac{1}{2J} x\right)},$$  \hspace{1cm} (5.9)

where
\[ x = \frac{g \mu_B J H_0}{k_B T}. \]  
\[ (5.10) \]

The magnetic moment of the sample of \( N \) atoms is
\[ M = N \langle \mu_z \rangle = N g \mu_B \langle J_z \rangle \]
\[ = \sum_{m=-J}^{J} \frac{m e^{m e^{-J}}}{Z_J(x)}. \]  
\[ (5.11) \]
\[ (5.12) \]

This expression can be reduced to the useful form
\[ M = N g \mu_B J B_J(x). \]  
\[ (5.13) \]
where \( B_J \) is the Brillouin function
\[ B_J(x) = \frac{2J+1}{2J} \coth \left( \frac{2J+1}{2J} x \right) - \frac{1}{2J} \coth \frac{x}{2J}. \]  
\[ (5.14) \]

Two extreme cases are considered:

(i) \( x \ll 1 \)

Note that \( M_o = N g \mu_B J \) is the maximum moment attainable for the sample if all atoms are exactly aligned, so that \( B_J(x) = M/M_o \) is the relative or reduced magnetization of the sample. For \( x \ll 1 \),
\[ M = \frac{J+1}{3J} x. \]  
\[ (5.15) \]

In general,
\[ M = \frac{N g^2 \mu_B^2 J (J+1)}{3k_B T} H_0, \]
\[ (5.16) \]

and the susceptibility \( \chi = M/H_0 \) is given by
\[ \chi = C / T \]  
\[ (5.17) \]
where
\[ C = \frac{N g^2 \mu_n^2 J (J + 1)}{3k_B} \]  

Eq. (5.18) is known as Curie’s law. It states that the susceptibility of a paramagnet is independent of the applied field (for fields sufficiently small that \( x \ll 1 \)) and inversely proportional to the absolute temperature.

(ii) \( x \to \infty \)

The other limiting case that is of particular physical interest is that of very large value of \( x \), in particular as \( T \to 0 \). Note that the two limiting cases correspond to situations in which the magnetic energy is much less than the thermal energy, and vice versa. For \( x \ll 1 \), the magnetic field is not very effective in aligning the magnetic moments because it is overwhelmed by thermal agitation, which tends to produce a random orientation of magnetic moments. On the other hand, when \( x \) is large, it is expected that significant alignment will occur, and the magnetic moment of the sample will approach its maximum. The reduced magnetization thus takes the form

\[ \frac{M}{Ng\mu_n J} = B_\delta (x) = 1 - \frac{1}{J} \exp \left( - \frac{g\mu_n H_o}{kT} \right) \quad \text{for} \quad x \gg 1 \]  

and

\[ \lim_{T \to 0} \frac{M}{Ng\mu_n J} = 1 \]  

The last equation shows that the magnetization reaches its maximum saturation value as \( T \to 0 \) even for infinitesimally small fields. For transition metals, \( J = S \). Fig. 5.2 shows the dependence of the reduced magnetization \( \sigma = M/M_o = M(T,H)/M(0,0) \) upon
\( \tilde{\mu} \frac{HS}{kT} \) for magnetic system in the non-interacting limit, as given by Eq. (5.13), where 

\( J \) is replaced by \( S \) (total spin) and \( \tilde{\mu} = g \mu_B \).

![Graph](image)

Fig. 5.2. Dependence of the reduced magnetization \( \sigma = M/M_o = M(T,H)/M(0,0) \) upon \( \tilde{\mu} \frac{HS}{kT} \) for magnetic system in the non-interacting limit, as given by Eq. (5.13), where 

\( J \) is replaced by \( S \) (total spin) and \( \tilde{\mu} = g \mu_B \).

### 5.3 Ferromagnetism

The simplest effective field approximation (mean-field theory) consists in considering only one magnetic atom and replacing its interaction with the remainder of the crystal by an effective field. The single atom Hamiltonian has the following form:

\[
\mathcal{H}_i = 2JS_i \cdot \sum_{j=1}^z S_j = -g \mu_B S_i \cdot \mathbf{H}_e
\]

(5.21)

where \( z \) is the number of nearest neighbors of the \( i^{th} \) atom, \( J \) is the exchange interaction, and \( \mathbf{H}_e \) is the effective magnetic field. The effective field then has the form:
\[ H_e = \frac{2J}{g\mu_B} \sum_j S_j. \]  

(5.22)

In the spirit of mean-field approximation, each \( S_j \) can be replaced by its average value \( \langle S_j \rangle \). As all magnetic ions are identical and equivalent, \( \langle S_j \rangle \) is related to the total magnetic moment by

\[ M = Ng\mu_B \langle S_j \rangle. \]  

(5.23)

Then,

\[ H_e = \frac{2zJ}{Ng^2\mu^2_B} M, \]

giving the molecular field coefficient \( \lambda \)

\[ \lambda = \frac{2zJ}{Ng^2\mu^2_B}. \]  

(5.24)

The total field acting on the \( i^{th} \) atom in the presence of an applied magnetic field is

\[ H = H_o + H_e. \]  

(5.25)

Following the same procedures as in Section 5.2, with \( H_o \) replaced by \( H \), the magnetic moment becomes

\[ M = Ng\mu_B SB_S \left( \frac{g\mu_B HS}{k_B T} \right) = Ng\mu_B SB_S (hS). \]

\[ M = M_0 B_S (hS) \]  

(5.26)

For \( hS \ll 1 \),

\[ M = \frac{Ng^2\mu^2_B S(S+1)}{3k_B T} H = \frac{CH}{T}. \]  

(5.27)

The susceptibility is given by
\[ \chi = \frac{M}{H_o} = \frac{C}{T - \theta} \]  
(5.28)

with

\[ \theta = \frac{2zJS(S + 1)}{3k_B} . \]  
(5.29)

Eq. (5.28) is known as Curie-Weiss law, and the parameter \( \theta \) is called the paramagnetic Curie temperature.

For lower temperatures, at which \( hS \) is not small compared to unity, Eq. (5.26) must be used. Because \( M \) appears in the argument of the Brillouin function as well as in the left-hand side of the equation, some numerical or graphical method of solution must be employed to obtain \( M(H,T) \). Fig. 5.3 shows both sides of Eq. (5.26) plotted as a function of \( M \). Eq. (5.26) possesses the trivial solution \( M = 0 \) for all values of \( T \), but there exists a second solution \( M \neq 0 \), if the slope of the right-hand side of Eq. (5.26) is larger than the initial slope of the left-hand side.

The general behavior of the spontaneous magnetization can be inferred without extensive calculations. The slope of the straight line is proportional to \( T \), and rotating the line about the origin corresponds to changing the temperature. When \( T \to 0 \), the reduced magnetization \( M/M_o \to 1 \), and the material becomes completely magnetized. As \( T \) is increased, the spontaneous magnetization is reduced and finally vanishes when the slope of the line is equal to the initial slope of the Brillouin function. The temperature at which this occurs evidently is the Curie temperature and is given by

\[ T_c = \frac{2zJS(S + 1)}{3k_B} = \theta \]  
(5.30)
Fig. 5.3. Plot of left-hand side and right-hand side of Eq. (5.26). $\lambda$ is the molecular field coefficient and $\beta = 1/k_B T$ (from Ref. 28).
Chapter 6: Magnetic Exchange Interactions

The system we consider consists of an array of parallel carbon nanotubes, known to form a regular hexagonal structure with nearest-neighbor distance equal to that between neighboring graphene sheets. Each nanotube is assumed to contain chains of magnetic ions.

It is found, as shown below, that the magnetic couplings between two adjacent nanotubes depend on the geometry (configuration) of the metal chains inside the tubes and on the relative position (site) between the metal and carbon atoms. We consider here only two types of chain configurations: straight chains and helix chains. Similar to Part I, four sites of metal atoms are considered: (i) directly above a C atom (top site), (ii) above the center of the hexagon (hole site), (iii) over a C-C bond (symmetric bond site) and (iv) over a C-C bond (asymmetric bond site) (see also Figs. 3.3, Part I). Fig. 6.1 shows the hole and bond sites. Since Fe, Co, and Ni have similar electronic structures, except for the d-electrons, we assume that the results (related to stable structures) obtained in Part I for Fe (stable configurations) also hold for Co and Ni (it is noted that CN(5,5) and CN(10,10) intercalated with Ni, where Ni atoms are outside the tube, were theoretically studied by Menon et al.,28 from their calculations, only the bond and top sites are stable;
in the present work, we consider the case of Ni atoms inside the nanotubes. In this study, we focus on the dependence of the magnetic couplings of the system on the geometry of the metal chain(s) and on the site(s) of the metal atom(s) relative to the neighboring carbon atoms.
Fig. 6.1. Different sites of Fe atoms relative to the CN surface: hole (a), bond (b)
Three kinds of magnetic interactions are present in this model system: the indirect exchange interaction between magnetic ions of neighboring nanotubes mediated by the electrons of these carbon nanotubes, the direct exchange interaction between magnetic ions along the axis of a nanotube, and the dipolar interaction. The indirect exchange between the ions within the same nanotube is neglected because it is much smaller than the direct exchange.

The direct exchange interaction arises from direct Coulomb interactions among electrons from two ions when their charge distributions overlap. The indirect exchange interaction, on the other hand, occurs when two magnetic ions are separated by a nonmagnetic ion (i.e., one with all electronic shells closed). In this case the magnetic interaction between two ions is mediated by conduction electrons of the nonmagnetic medium (see Figs. 6.2a and 6.2b)

![Diagram showing magnetic ions and their charge distributions.](image)

Fig. 6.2a. Direct exchange: magnetic ions interact because their charge distributions overlap.
Fig. 6.2b. Indirect exchange: in the absence of the direct exchange between the magnetic ions, an indirect exchange interaction between the magnetic ions is mediated by the conduction electrons of the medium.

6.1 Indirect Exchange Interaction

The indirect exchange depends on two factors: the magnetic moment and the nature of the medium. Since there are two types of CN's, metallic and semiconducting, two types of indirect exchange are considered: indirect exchange in metallic CNs, and indirect exchange in semiconducting CN's.

6.1.1 Indirect Exchange in Metallic Carbon Nanotubes

The indirect exchange interaction is an effective one, which depends on temperature and the separation between two magnetic ions for both metallic and semiconducting carbon nanotubes. For metals, at absolute temperature $T = 0$, it is given by

$$J = \frac{J^2 \Omega^2 m^*}{16\pi^3 \hbar^2 r^4} \left[ \sin(2k_F r) - 2k_F r \cos(2k_F r) \right],$$

(6.1)
with $r$ the distance between two magnetic ions, $\hbar$ Planck’s constant divided by $2\pi$, $k_F$ the Fermi wave vector, $m^*$ the effective mass, $\Omega$ the volume of the atomic cell, and $\overline{J^2}$ a weighted average, where $J$ is the exchange integral between an electron of the magnetic shell and a conduction electron.

For $T > 0$, the indirect exchange interaction per unit volume in Eq. (6.1) generalizes to

$$ J(T) = \frac{V^2}{2} \left( \frac{J}{N\mu_B} \right)^2 \chi_T(r), $$

with $V$ the unit cell volume, $N$ the total number of atoms per unit cell, $\mu_B$ the Bohr magneton, and $\chi_T$ the temperature-dependent susceptibility per unit volume given by

$$ \chi_T(r) = \frac{m^* \mu_B^2}{4\pi^3 \hbar^2 r^2} e^{-2\eta_n r \sin \varphi_n} \left[ \frac{\sin(2\eta_o r \cos \varphi_o)}{2r^2} \frac{\eta_o \cos(2\eta_o r \cos \varphi_o + \varphi_o)}{r} \right. $$

$$ - \frac{2\pi}{\gamma} \cos(2\eta_o r \cos \varphi_o) - \frac{4\pi^2 r}{3\eta_o \gamma^2} \cos(2\eta_o r \cos \varphi_o - \varphi_o) \left. \right], $$

where $\eta_n$, $\varphi_n$, $\beta$, and $\gamma$ are defined by

$$ \eta_n = \left\{ k_F^2 + \left[ 2(2n + 1) \frac{\pi}{\gamma} \right]^2 \right\}^{1/4}, $$

$$ \varphi_n = \frac{1}{2} \arctan \left[ 2(2n + 1) \frac{\pi}{\gamma k_F^2} \right], $$
\[ \gamma = \frac{\hbar^2}{m^* k_B T}, \quad (6.5) \]

with \( k_B \) Boltzmann's constant.

Fig. 6.2 shows a plot of the indirect exchange interaction as a function of distance between two magnetic ions, for different temperatures.

![Graph showing indirect exchange interaction as a function of distance for different temperatures.]

Fig. 6.3. Indirect exchange of Fe in CN(8,8) as a function of distance \( r \) at two different temperatures.

### 6.1.2 Indirect Exchange in Semiconducting Carbon Nanotubes

For semiconducting carbon nanotubes, the indirect exchange interaction between two magnetic atoms a distance \( r \) apart, due to thermally excited electrons, is given by\(^{32}\)

\[ J(T) = \frac{\bar{J}^2 \Omega^2 m^* n(T) e^{1}}{2 \pi \hbar^2} \frac{1}{r} \exp \left[ -\left( \frac{2k_B T m^*}{\hbar^2} \right) r^2 \right], \quad (6.6) \]

where \( n(T) \) is the conduction electron density of the medium, equal to
\[ n(T) = \frac{m^{3/2}}{2\pi^2} \left( \frac{2k_B T}{\hbar^2} \right)^{3/2} F_{1/2}(\eta), \]  
(6.7)

with \( \eta \) the degeneracy of the electron gas and \( F_{1/2}(\eta) \) a tabulated function. As seen from Eqs. (6.6) and (6.7) \( J(T) \) is always positive.

In semiconducting carbon nanotubes, another indirect exchange interaction, due to the virtual excitations of electrons from the valence band to the conduction band, also takes place and is given by \(^{33}\)

\[ J_{ij} = \frac{J^2}{2\pi^3h^2r_{ij}^4} \left[ \sin(k_ir_{ij}) - k_ir_{ij}\cos(k_ir_{ij}) \right] \exp \left[ -\frac{(2m^*E_g)^{1/2}}{\hbar}r_{ij} \right], \]  
(6.8)

with

\[ k_i = 2\pi(3/4\pi\Omega)^{1/3}; \]  
(6.9)

\( r_{ij} \) is the distance between magnetic atoms at sites \( i \) and \( j \) of the lattice formed by the magnetic ions. \( J_{ij} \) due to virtual excitations of electrons can be positive or negative.

### 6.2 Direct Exchange Interaction

In contrast to the indirect exchange interactions given by Eqs. (6.3) to (6.5) and Eqs. (6.6) and (6.8), the direct exchange interaction is temperature-independent and, in a model of localized magnetic moments, is determined by Rushbrooke and Wood's formula \(^{34}\)

\[ \frac{k_BT_c}{J_{direct}} = \frac{5}{96} (z-1)[11S(S-1)-1], \]  
(6.12)
with \( z \) the number of nearest neighbors, \( J_{\text{direct}} \) the direct exchange interaction, \( S \) the total spin, and \( T_C \) the Curie temperature.

### 6.3 Magnetic Dipolar Interaction

The magnetic atoms are also coupled by the classical dipolar interaction. The energy between magnetic moment \( \mu_i \) and \( \mu_j \) is determined by\(^{35} \)

\[
E_{\text{dip}} = -\mu_j \cdot B_j
\]

\[
= \frac{\mu_i \cdot \mu_j - 3(\mu_i \cdot n_y)(\mu_j \cdot n_y)}{r_j^3}
\]

\[
= -D_y \left[ S_i \cdot S_j - 3 \left( S_i \cdot \hat{n}_y \right) \left( S_j \cdot \hat{n}_y \right) \right]
\]

where \( \hat{n}_y \) denotes the unit vector along the direction that connects the magnetic moments \( m_i \) and \( m_j \), and \( D_y = -g^2 \mu_B^2 / r_j^3 \). Fig. 6.3 illustrates the classical magnetic dipolar interaction between two dipoles.
Fig. 6.4 Classical magnetic dipolar interaction between two dipoles.
Chapter 7: Magnetic Phase Transitions

and Long Range Magnetic Order

The molecular-field approximation for temperature-independent interaction has been discussed in chapter 6. Its generalization to temperature-dependent interaction with nearest-neighbor assumption is next presented. The Heisenberg Hamiltonian for our model system is

\[ H = -2 \left[ \sum_{i \neq j, \text{intra tube}} J_{ij}^{\text{direct}} S_i S_j + \sum_{k \neq l, \text{inter tube}} J_{kl}^{\text{indirect}} (T) S_k S_l \right], \]  

(7.1)

where \( J_{ij}^{\text{direct}} \) is the direct exchange interaction between two atomic spins at sites \( i \) and \( j \) inside a given carbon nanotube, \( J_{ij}^{\text{indirect}} \) is the indirect exchange interaction between two atoms in two neighboring carbon nanotubes, and \( S_i \) and \( S_j \) are the spins of atoms \( i \) and \( j \), respectively.

The mean-field theory of temperature-independent interactions\(^{36,37}\) is next generalized for the case of temperature-dependent interactions. In the absence of an external field, the one-spin cluster Hamiltonian is
\[
H = -2 \left[ \sum_{i<j, \text{ intratube}} J_{ij}^{\text{direct}} S_i \langle S_j \rangle + \sum_{k<l, \text{ intertube}} J_{kl}^{\text{indirect}}(T) S_k \langle S_l \rangle \right], \tag{7.2}
\]

which yields a temperature-dependent molecular field parameter

\[
\lambda(T) = \frac{2 \left[ \sum_{j} J_{ij}^{\text{direct}} + \sum_{l} J_{il}^{\text{indirect}}(T) \right]}{Ng^2\mu_B^2}, \tag{7.3}
\]

with \( g \) the Landé factor and \( \mu_B \) the Bohr magneton, so that the critical temperature is given by the solution of the implicit equation

\[
T = \frac{2}{3k_B} S(S+I) \max_{k} \hat{J}_T(k), \tag{7.4}
\]

where \( k \) is a wave vector and

\[
\hat{J}_T(k) = \sum_{j, \text{ intratube}} J_{ij}^{\text{direct}} \exp(ik \cdot r_j) + \sum_{l, \text{ intertube}} J_{il}^{\text{indirect}}(T) \exp(ik \cdot r_l). \tag{7.5}
\]

As discussed in Part I, for the case of CN's filled with Fe atoms, \( J_{ij}^{\text{direct}} \) is ferromagnetic. \( J_{ij}^{\text{indirect}} \) however can be ferromagnetic or antiferromagnetic, depending on the magnitude of the Fermi wave vector of the medium in the presence of the doped materials and on the distance between two magnetic ions. These two factors in turn depend on the chain configurations, and on the diameter as well as on the chirality of the considered CN’s. Provided that \( J_{ij}^{\text{indirect}} \) is ferromagnetic (this can be achieved by performing the computation for various chain configurations and tube sizes, and only those configurations giving ferromagnetic couplings are chosen), it follows that all magnetic couplings are positive at all temperatures, so that the critical temperature is given implicitly by
\[ T_c = \frac{2}{3k_B} S(S+1) \left[ \sum_j J^{\text{direct}}_{jj} + \sum_l J^{\text{indirect}}_{ll}(T) \right]. \] (7.6)

The spontaneous magnetization \( M \) is given by the solution of the implicit equation
\[ M = M_0 B_S \left( \beta g \mu_B S \lambda(T) M \right), \] (7.7)
where \( M_0 \) is the saturated value of \( M \) and \( B_S \) is the Brillouin function. We note that Eq. (7.7) is formally equivalent to the corresponding equation for the case of temperature-independent interactions, with the essential difference being that the molecular field parameter \( \lambda \) appearing in Eq. (7.7) is now temperature-dependent.

The magnetic properties of doped carbon nanotubes depend on several factors. First, as a result of charge transfer (from metal to carbon or vice versa), there is a Fermi energy shift, leading to a change in the Fermi wave vector \( k_F \) of the nanotube. For Ni, the direction and amount of charge transfer depend on the tube diameter, the metal sites, and the nature of the bonding between the tube and the metal ion (ionic or covalent).\textsuperscript{28} For Fe, our results (see Part I) show that there is always a net charge transfer from Fe to the nanotubes CN(8,0) and CN(12,0). Because of the much higher cost of computation and the problem of computer memory, computation for systems larger than those considered (CN(8,0) and CN(12,0)) are not performed. Because of these reasons, the Fermi wave vectors of nanotubes of different sizes are determined as follows: theoretical calculations predict that near the Fermi level a universal density of states exists and depends, to first-order, only on the metallic or semiconducting character of the nanotube\textsuperscript{38-40}. The Fermi energy shift is therefore expected to be approximately the same for all metallic nanotubes considered here. The Fermi energy shift is taken to be 0.4 eV and 1.1 eV for
semiconducting and metallic carbon nanotubes, respectively (the approximate values of Fermi energy shift are based on Part I and on Refs. 32, 14, 15 and 40). Because the low energy \( \pi \)-band is hardly affected by intercalation,\textsuperscript{13-14} the new values of \( k_F \) are determined in first order by assuming that the band structure of the carbon nanotube after doping is unchanged except for the Fermi energy shift. The energy dispersion of metallic nanotubes can be constructed from the formula:\textsuperscript{41}

\[
E(k_x, k_y) = +\gamma_0 \left[ 1 + 4 \cos \left( \frac{\sqrt{3} k_x a}{2} \right) \cos \left( \frac{k_y a}{2} \right) + 4 \cos^2 \left( \frac{k_y a}{2} \right) \right]^{1/2},
\]

where \( \gamma_0 \) is the energy overlap integral between nearest neighbors, \( k_x \) and \( k_y \) are wave vectors in the \( x \)- and \( y \)-direction, and \( a \) is C-C the bond length.

Another factor that strongly influences the magnetic properties of doped carbon nanotubes is the location of transition metal atoms inside the nanotubes. We consider only the two energetically favorable sites of metal atoms: the hole and the bond sites. Corresponding to these sites, several helical configurations are possible depending on the helix angle. Figs. 7.1a and 7.1b illustrate a few representative hole and bond sites of Fe atoms. In Fig. 7.1, the abbreviations B and H stand for bond and hole sites, respectively. The height \( z \) of the adatoms above the carbon layer is taken to be 1.52 and 1.92 Å (see Part I and Ref. 22) for the hole and bridge sites, respectively. Depending on the chain geometry (helix or straight), helix angle (for helix chains), and ion-ion separation, the interaction between metal atoms inside a given nanotube can be of the direct or indirect type. Moreover, the indirect exchange interaction can be either ferromagnetic or antiferromagnetic. For iron-doped carbon nanotubes, we consider two typical bridge-sites: polymeric\textsuperscript{42} (interatomic separations from 1.96 to 2.47 Å) and well-separated
(interatomic separations from 3.1 to 4.7 Å), respectively. While the interatomic interaction in a given nanotube of the former type is of the direct exchange type, the coupling in the latter is of the indirect exchange type. The direct interaction is ferromagnetic (see Part I and Ref. 43). The indirect exchange interaction, which is ferromagnetic in this case, is determined by RKKY theory.

Next, as a result of the interaction between the transition metal atoms and the carbon nanotube, depending on the metal types, there is a change in total magnetic moments of transition metal atoms compared to the isolated ones. It was found that the total magnetic moment per atom decreases for the cases of magnetic transition metal atoms adsorbed on graphite\textsuperscript{21, 22} and Ni adsorbed on carbon nanotubes.\textsuperscript{28} Our results from Part I show that for the case of a single Fe atom inside and outside the nanotube, a reduction of total magnetic moment is observed only when the Fe atom is at the hole position. Therefore, the value of the total magnetic moment of an Fe atom is taken to be 2.0\(\mu_B\) and 4.0\(\mu_B\) for an Fe atom located at the hole and bond positions, respectively. For Co and Ni, the total magnetic moments are assumed to be the same as those in Refs. 21 and 28, respectively. The values of the intra-atomic interaction \(J\) are 1.0 eV, 1.0 eV, and 0.39 eV for Fe, Co, and Ni, respectively.\textsuperscript{32, 44, 45}
Fig. 7.1a. Various top and bond configurations for an armchair \((m,m)\) nanotube. B and H are the abbreviations for the bond and hole sites, respectively.
Fig. 7.1b. Various top and bond configurations for a zigzag \((n, 0)\) nanotube. B and H are the abbreviations for the bond and hole sites, respectively.
7.1 Results and Discussion

The indirect exchange between adjacent nanotubes is much weaker than the direct exchange inside the nanotube. The ratio $J^\text{indirect} / J^\text{direct}$ is found to vary approximately from $10^{-4}$ to $10^{-3}$ for the polymeric configuration, and the ratio $J_1/J_2$, where $J_1$ is the nearest-neighbor indirect exchange in each tube and $J_2$ is the nearest-neighbor exchange between adjacent tubes, is found to range from $5.0 \times 10^{-3}$ to $8.0 \times 10^{-2}$. Therefore, it is expected that the values of $T_c$ of the systems considered are mainly determined by the direct exchange interactions. For the isolated atom configuration, only the indirect interaction exists because the M-M bond length, where M denotes a metal, is too large for direct exchange. Keeping in mind that one-dimensional systems with short-range interactions do not exhibit long-range order at nonzero temperature when all fluctuations are taken into account (unlike in the present mean-field treatment), it is seen that even though the indirect interaction is small, a nonzero critical temperature still obtains as long as the indirect interaction does not vanish.

We consider carbon nanotubes of indices (10, 10), (8, 8), (6, 6), (18, 0), (8, 0), and (9, 0), where (8, 0) is semiconducting, and the others are metallic. Fig. 7.2 illustrates the graphical solution of Eq. (7.6) for the critical temperature $T_c$, and also shows the corresponding reduced spontaneous magnetization $M/M_0$ for a single chain of Fe atoms inside (10, 10) metallic carbon nanotubes. Table 7.1 lists the values of the critical temperature for (10,10) and (6,6) metallic carbon nanotubes filled with one or nine chains of various magnetic elements (Fe, Co, and Ni). $T_c$ is highest for the case of Co and lowest for the case of Ni. Room or higher critical temperatures can be reached with higher loading; for example, for the case of CN(6,6), the $T_c$ values increases from
352.5°K to 705.6 °K as the number of chains increases from one to nine. Both direct and indirect exchange interactions are present in these cases.

Table 7.2 presents values of $T_c$ for nanotubes of varying diameters and chirality. These values are determined for various chain geometries and atom sites. For a given nanotube type, e.g., (10,10), different $T_c$ values are obtained for different chain geometries and atom sites. Also, nanotubes of different diameters or chirality yield different $T_c$'s. As expected, the values of $T_c$ are low since only indirect exchange (weak interaction) is present for these cases.

It should also be noted that for two-dimensional arrays of carbon nanotubes, the anisotropy of the spin of the encapsulated magnetic elements is essential to ensure long-range ferromagnetic order, since isotropic two-dimensional systems with short-range forces are well known not to exhibit long-range order.

Finally, whether the system becomes ferromagnetic or antiferromagnetic is very sensitive to the metal-metal bond length. For example, for the (10, 10) nanotube, the indirect exchange interactions between nearest and next-nearest Fe atoms in B1 to B4 (Fig. 7.1) configurations, which are not listed in Tables 7.1 and 7.2, are antiferromagnetic.
Fig. 7.2. An example of the graphical solution for the critical temperature for the Fe-CN(10,10) system.
Table 7.1. \( T_c \) values for (10, 10) and (6, 6) nanotubes filled with one or more chains of Fe. \( N_c \) is the number of chains; \( r \) is M-M bond length in Å; \( z \) is the distance between metallic atom and carbon surface.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Diameter (Å)</th>
<th>Index</th>
<th>( N_c )</th>
<th>Configuration</th>
<th>( z ) (Å)</th>
<th>( r ) (Å)</th>
<th>( T_c ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>13.56</td>
<td>(10,10)</td>
<td>1</td>
<td>helix, bond</td>
<td>1.92</td>
<td>1.96</td>
<td>352.5</td>
</tr>
<tr>
<td>Co</td>
<td>13.56</td>
<td>(10,10)</td>
<td>1</td>
<td>helix, bond</td>
<td>1.92</td>
<td>1.96</td>
<td>512.38</td>
</tr>
<tr>
<td>Ni</td>
<td>13.56</td>
<td>(10,10)</td>
<td>1</td>
<td>helix, bond</td>
<td>1.77</td>
<td>1.99</td>
<td>52.79</td>
</tr>
<tr>
<td>Fe</td>
<td>8.138</td>
<td>(6,6)</td>
<td>1</td>
<td>helix, bond</td>
<td>1.92</td>
<td>2.47</td>
<td>353.95</td>
</tr>
<tr>
<td>Fe</td>
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<td>(6,6)</td>
<td>9</td>
<td>straight</td>
<td>1.92</td>
<td>2.15</td>
<td>705.60</td>
</tr>
</tbody>
</table>

Table 7.2. \( T_c \) values for nanotubes of different diameters or chirality, filled with one chain of Fe of various configurations (see Fig. 7.1 for corresponding configurations).

<table>
<thead>
<tr>
<th>((m,n))</th>
<th>Diameter (Å)</th>
<th>Site</th>
<th>( z ) (Å)</th>
<th>Chain</th>
<th>( r ) (Å)</th>
<th>Loading</th>
<th>( T_c ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10,10)</td>
<td>13.56</td>
<td>B6</td>
<td>1.92</td>
<td>Helix</td>
<td>3.99</td>
<td>MC(_{40})</td>
<td>116.54</td>
</tr>
<tr>
<td>(8,8)</td>
<td>10.85</td>
<td>B6</td>
<td>1.92</td>
<td>Helix</td>
<td>3.94</td>
<td>MC(_{32})</td>
<td>43.42</td>
</tr>
<tr>
<td>(18,0)</td>
<td>14.10</td>
<td>B4</td>
<td>1.92</td>
<td>Helix</td>
<td>4.35</td>
<td>MC(_{54})</td>
<td>163.06</td>
</tr>
<tr>
<td>(18,0)</td>
<td>14.10</td>
<td>B6</td>
<td>1.92</td>
<td>Helix</td>
<td>3.89</td>
<td></td>
<td>19.28</td>
</tr>
<tr>
<td>(8,0)</td>
<td>6.26</td>
<td>B4</td>
<td>1.92</td>
<td>Helix</td>
<td>3.73</td>
<td>MC(_{32})</td>
<td>8.38</td>
</tr>
<tr>
<td>(9,0)</td>
<td>7.05</td>
<td>B4</td>
<td>1.92</td>
<td>Helix</td>
<td>4.30</td>
<td>MC(_{27})</td>
<td>34.8</td>
</tr>
<tr>
<td>(10,10)</td>
<td>13.56</td>
<td>H1</td>
<td>1.52</td>
<td>Helix</td>
<td>4.08</td>
<td>MC(_{30})</td>
<td>43.08</td>
</tr>
<tr>
<td>(10,10)</td>
<td>13.56</td>
<td>H2</td>
<td>1.52</td>
<td>Helix</td>
<td>4.04</td>
<td>MC(_{60})</td>
<td>41.42</td>
</tr>
<tr>
<td>(10,10)</td>
<td>13.56</td>
<td>H3</td>
<td>1.52</td>
<td>Straight</td>
<td>4.92</td>
<td>MC(_{70})</td>
<td>32.82</td>
</tr>
<tr>
<td>(8,8)</td>
<td>10.85</td>
<td>H1</td>
<td>1.52</td>
<td>Helix</td>
<td>3.87</td>
<td>MC(_{24})</td>
<td>15.84</td>
</tr>
<tr>
<td>(18,0)</td>
<td>14.10</td>
<td>H2</td>
<td>1.52</td>
<td>Helix</td>
<td>4.67</td>
<td>MC(_{72})</td>
<td>41.26</td>
</tr>
<tr>
<td>(8,0)</td>
<td>6.26</td>
<td>H2</td>
<td>1.52</td>
<td>Helix</td>
<td>3.22</td>
<td>MC(_{32})</td>
<td>8.53</td>
</tr>
<tr>
<td>(9,0)</td>
<td>7.05</td>
<td>H2</td>
<td>1.52</td>
<td>Helix</td>
<td>4.48</td>
<td>MC(_{36})</td>
<td>13.74</td>
</tr>
</tbody>
</table>
7.2 Suggestions for Future Work

The determination of the exchange interactions and the critical temperature is subject to several approximations. First, mean-field theory overestimates $T_c$ because of its neglect of some fluctuations. Second, the isotropic RKKY model is applied to an anisotropic system of carbon nanotubes. Next, the electrons in very long nanotubes are correlated (Luttinger liquid)$^{46}$ while the RKKY model is appropriate for noncorrelated electron. In addition, a small increase in $T_c$ arises from the fact that Fermi surfaces more realistic than the spherical ones used to derive Eqs. (5.31)-(5.33) and (5.39) lead to slower decaying indirect exchange interactions, and thus to higher critical temperatures. Also, the effect of a finite electron mean-free path,$^{47}$ in contrast to the infinite one assumed here, and the effects of surface curvature on the bonding features of carbon nanotubes and metal atoms, have not been taken into account. These effects will be investigated in forthcoming studies. In addition, the study of antiferromagnetism of the Fe-CN systems would be an interesting project.
Part III

Computer Simulation of Depletion Effects in
Three-Dimensional Colloid-Polymer Systems
Chapter 8: Introduction

The use of colloids is widespread in classical applications (such as paints, coatings, tires, inks, etc...) as well as in new technological applications, which include colloidal processing of ceramics\(^1\), colloidal crystals for photonics bandgap materials,\(^2\) porous metallic nanostructures,\(^6\) magnetic colloidal nanoparticales for medical diagnosis,\(^7\) colloidal inks for directed assembly of mesoscale periodic structures,\(^9\) and colloidosomes for encapsulation.\(^10\) In such applications, soluble or adsorbing polymers are commonly added to control the stability and rheological properties of the colloidal dispersions.\(^11\)

Colloid-polymer systems play an important role in technological applications in which the surface effects dominate. Classical examples of such applications include wetting (surface treatment, lubrication, adhesion,...), multiphase flows (distillation columns, oil transportation,...), mineral floatation, liquid-liquid extractions, foams, emulsions, processing of nanoparticles, and numerous biological and pharmaceuticals. More recent applications involve particulate two-dimensional arrays in optics, optoelectronics, nano-lithography, microcontact printings, fabrications of nanostructured surfaces for catalytic films and solar cells, usage of two-dimensional protein crystals for immunosensors, and isoporous ultrafiltration membranes for bioelectronic and biophotonic devices.\(^12\)
It is well-known that the addition of soluble polymer to colloidal dispersions, even in a small amount, has a drastic effect on the phase behavior, mainly because it induces a new type of interaction between the colloidal particles, the depletion interaction (see Fig. 8.1). At appropriate concentrations and for a suitable ratio of the size of the polymer to that of the colloid, the depletion interaction occurs as a result of an imbalance in osmotic pressure arising from the exclusion of polymer from the region between two colloid particles when their surface-surface separation becomes smaller than the diameter of a free polymer coil. At a high enough concentration of polymer, this depletion interaction may lead to phase separation.

![Diagram](image.png)

**Fig. 8.1.** The depletion of polymer in the overlapping region between two spheres as they approach each other results in an imbalance in osmotic pressure, which leads to an attractive force called the depletion force (from ref. 16).

Depletion phenomena and depletion-induced phase separation are extensively studied and the subject of many fundamental studies, especially of phase transitions. In the earliest model of colloid-polymer systems, that of Asakura and Oosawa (AO) model,
colloidal particles are taken as hard spheres, and the polymer molecules are approximated as effective spheres of fixed radius and assumed to interpenetrate each other freely (penetrable hard sphere approach or PHS). The range of this effective interaction is equal to the size of the macromolecules, and the strength of the attraction is proportional to the osmotic pressure of these. Because of its simplicity, although this model captures some aspects of real colloid-polymer systems,\textsuperscript{20-24} it misses several key aspects as well.\textsuperscript{21,25} In particular, it is inapplicable to the case of larger polymer-to-colloid size ratio, $q$ ($q = R_g / R_c$, where $R_c$ is the radius of colloid; $R_g$ is the mean-square distance of all monomers from the center of mass of the polymer).

Independently, and more than twenty years later, Vrij\textsuperscript{27} showed that attractive interactions induced between the colloids in colloid-polymer mixtures are due to the presence of the non-adsorbing polymers. He used the same PHS approach as Asakura and Oosawa. The polymers are excluded by a center-of-mass distance of $(R_c + R_g)$ from the colloids. In the same study, Vrij also presented experimental evidence for fluid-fluid separation in a mixture of silica particles and polystyrene.\textsuperscript{27}

A few years later, Gast \textit{et al.}\textsuperscript{28} further extended the PHS theory by proposing a pairwise perturbation theory for the free energy of a mixture of colloids and PHSs. Using the hard-sphere system as a reference, they calculated the phase diagram from the free energy and determined the nature (i.e., colloidal gaseous, liquid, or solid) of the coexisting phases. Gast \textit{et al.} predict fluid-solid coexistence when the polymer-to-colloid size ratio $q$ is much smaller than 1, with the gas-liquid branch lying inside the unstable regions. Upon increasing the ratio $q$, the gas-liquid coexistence curve becomes stable.
The dependence of the nature of the coexisting phases on the size ratio \( q \) became clearer from the work of Lekkerkerker et al.,\(^{24-29}\) who used a semi-grand canonical treatment to develop an osmotic equilibrium model for a colloid-polymer mixture, taking into account the effective accessible volume for PHSs. In this theory, polymer molecules are partitioned between the phases, and a polymer-colloid mixture is in equilibrium with a polymer solution, separated by a semi-permeable membrane that is permeable to polymer molecules. The resulting phase diagrams calculated by Lekkerkerker et al. showed that for a polymer-to-colloid size ratio \( q \) less than 0.3, a liquid-solid phase transition is observed, whereas for ratios of \( q \) greater than 0.3, three phases can occur: two different fluid phases (a gas-like phase and a liquid-like phase) and one solid phase.

The osmotic equilibrium theory for colloid-polymer mixtures was tested with computer simulation on a dispersion of spheres immersed in a solution of ideal lattice polymer chains by Meijer and Frenkel.\(^{30}\) Their simulation results agree well with the theory of Lekkerkerker et al for small values of \( q \). Deviations appear, however, for larger values of \( q \) (when the radius of gyration of the polymer has the same order of magnitude as the colloid radius). The discrepancies clearly result from the fact that properties of polymer are oversimplified as they are regarded as ideal and penetrable hard spheres.

In contrast to the PHS approach, the theory proposed by de Gennes,\(^{31,32}\) takes into consideration the polymer interactions by introducing the excluded volumes of the polymer segments. The inclusion of these interactions gives insight into the details of polymer configurations. de Gennes considered the contact potential between two colloidal spheres in a semi-dilute polymer solution in a good solvent for two limiting cases. For very large spheres, where the only relevant length scales are the colloidal
radius $R_c$ and the correlation length $\xi$, the scaling relation for the attractive potential between two colloidal spheres takes the form:

$$\frac{W}{k_B T} \approx \frac{R_c}{\xi}$$  \hspace{1cm} (8.1)$$

where $\xi$ is a function of polymer concentration $c$, and $\xi(c) = a(c^3)^{-3/4}$, with $a$ being the size of the monomer. As $R_c \gg \xi$, the attraction between two spheres is predicted to be very substantial.

In the second case where $R_c \ll \xi$, the contact potential is\textsuperscript{33}

$$\frac{W}{k_B T} \approx \left( \frac{R_c}{\xi} \right)^{\frac{4}{3}}$$  \hspace{1cm} (8.2)$$

For $R \ll \xi$, a very weak attractive potential is expected.

The concepts of de Gennes were further elaborated by Odijk,\textsuperscript{34,35} who derived a very simple shape of the profile of the polymer segment concentration in a semi-dilute polymer solution around a very small sphere. He also calculated the osmotic virial coefficient between polymer and colloid for $R_g \ll R_c$ ($R_g$ and $R_c$ are defined as before) and concluded that no phase separation is expected on mixing very long chains with very small colloidal spheres.

Compared to previously discussed models (PHS), the theories developed by de Gennes and Odijk clearly allow for the prediction of phase behavior of colloid-polymer mixtures for a larger range of $q$, from the "colloid limit" (very large colloid and very small polymer) to the "protein limit" (very small colloid and very large polymer). Their prediction that no phase transition occurs as $q \to \infty$ is an intriguing one: it is noted that the mere presence of attractive force (whether of depletion type or not) is however not
sufficient to induce liquid-liquid phase separation. As the polymer chain gets longer and the colloid smaller, the depletion effect will be drastically weakened.\textsuperscript{31-33} By analogy with simpler systems such as one-component fluids with short-range attractions, it is natural to suggest the absence of liquid-liquid phase equilibria at the limit $q \to \infty$, as found in some calculations.\textsuperscript{33,36} However, more recent calculations indicate the existence of a long-ranged tail of the depletion layer in the extreme "protein limit", which leads to phase separation.\textsuperscript{37} Special care must be exercised to shed light on this issue, because the occurrence of liquid-liquid coexistence in colloid-polymer systems is known from experiment and theory to be sensitive to the details of the polymer interactions as well as to the quality of the solvent.\textsuperscript{38-42}

The contradiction in predictions on phase behavior of the polymer-colloid mixtures at the "protein limit" from the different theories mentioned above indicates that this issue is not solved yet. We therefore propose to use computer simulation to shed light on this the problem. In order to clarify this controversial issue and to study the effect of the polymer-colloid size ratio on the phase behavior of colloid-polymer systems, we have systematically studied in detail the phase diagrams of colloid-polymer systems in three dimensions by using grand canonical histogram-rewriting Monte Carlo simulation combined with finite-size scaling for various polymer-to-colloid size ratios ranging from the "colloid limit" to the "protein limit." The effect of colloid-to-monomer size ratios on phase diagrams is also investigated, and scaling is used to determine the critical parameters at infinite polymer chain length.
In Chapter 9, the models and simulation methods are presented. Chapter 10 and 11 give the simulation results and a detailed discussion of the phase behavior upon the variation of the colloid-polymer size and colloid-to-monomer size ratios.
Chapter 9: Model and Simulation Methods

9.A Simulation Methods

One popular simulation method for studying the multiphase behavior of fluid systems is the Gibbs ensemble Monte Carlo (GEMC) simulation technique introduced by Panagiotopoulos. In the GEMC method, the two coexisting phases separate into two physically detached but thermodynamically connected boxes, the volume of which are allowed to fluctuate under a constant pressure environment. Measurements of the particle density in each box provide estimates of coexistence densities. The strength of the GEMC method lies in its elimination of the physical interface between the coexistence phases, the large free energy of which plagues conventional grand canonical simulations of phase coexistence in the form of long lived metastable states and extended tunneling times.

In the neighborhood of the critical point, however, and for reasons discussed in the Refs. 44-47, the GEMC method cannot be relied upon in providing accurate estimates of the coexistence-curve parameters. Finite finite-size scaling techniques, on the other hand, provide a highly effective route to infinite volume critical parameters from simulations of finite sizes. Their use has been extended to fluids by explicitly
incorporating the consequences of the lack of symmetry between the coexisting phases.\textsuperscript{49,51} This reduced symmetry of fluids with respect to magnetic systems such as the Ising model is manifest in the so-called "field-mixing" phenomenon which is a crucial behavior of fluids.

Besides the progress in extending the application of finite-size scaling concepts to fluid systems, another recent technical advance in computer simulation methods also greatly improves the efficiency with which one can tackle both the critical and subcritical regimes of model systems: the histogram reweighting technique.\textsuperscript{52-54} This technique hinges on the observation that histograms of observables accumulated at one set of model parameters can be reweighted to yield estimates for histograms appropriate to another set of parameters. The histogram reweighting method has been found to be especially profitable close to the critical point where, owing the large fluctuations, a single simulation affords reliable extrapolations over the entire critical region. Because of these advantages, in the present work, the grand canonical Monte Carlo (MC) simulation combined with finite-size scaling and histogram-reweighting methods is employed to determine the phase diagrams and critical parameters for the polymer-colloid mixtures. These methods will next be briefly described as they apply to the problems of interest in this study.

\subsection*{9.A.1 Grand Canonical Monte Carlo Simulation}

For the purpose of illustration, grand canonical Monte Carlo simulation method for a fluid of one component will be described. The method is then extended to a mixture consisting of two components.
One way of performing a MC simulation is to employ the grand canonical ensemble, in which, for a given volume $V$, the total configuration energy $E$, and particle number $N$ are allowed to fluctuate, but with average values determined by prescribed values of the temperature $T$ and the chemical potential $\mu$. The later two variables span the phase diagram, and by tuning their values, phase transition can be induced between the gas, liquid, and solid phases.

An outline of a MC implementation of the grand canonical ensemble is given in Fig. 9.1. Fluctuations in the energy and particle number occur by means of insertion and deletion. MC updates consist of either an insertion or a deletion attempt, which are chosen with equal probability. For an insertion, a random position in the system is chosen, and the energy change $\Delta E_I$ associated with placing a new particle at that position is calculated. The trial insertion is accepted with a probability given by a Metropolis rule designed to maintain detailed balance, a necessary condition for attaining thermodynamic equilibrium:\textsuperscript{55}

$$p_{acc}(N \rightarrow N + 1) = \min \left[ 1, \frac{ZV}{(N + 1)} \exp(-\beta \Delta E_I) \right], \quad (9.1)$$

where $Z = \exp(\beta \mu)$, $\beta = 1/k_BT$, and $N$ is the total number of particles.

Similarly, for a particle, we choose a particle at random from those present, calculate the energy change $\Delta E_D$ associated with its removal, and then perform the removal with probability given by

$$p_{acc}(N \rightarrow N - 1) = \min \left[ 1, \frac{N}{ZV} \exp(-\beta \Delta E_D) \right], \quad (9.2)$$
<table>
<thead>
<tr>
<th>PROGRAM MCGC</th>
<th>μVT ensemble simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>do icycle = 1, ncycle</td>
<td>perform ncycle MC cycles</td>
</tr>
<tr>
<td>ran = int(ranf()*(ndisp+nexc)) + 1</td>
<td></td>
</tr>
<tr>
<td>if (ran.le.npart) then</td>
<td>displace a particle</td>
</tr>
<tr>
<td>call move</td>
<td></td>
</tr>
<tr>
<td>else</td>
<td>exchange a particle with the reservoir</td>
</tr>
<tr>
<td>call exc</td>
<td></td>
</tr>
<tr>
<td>if (mod (icycle, nsamp).eq.0)</td>
<td>sample averages</td>
</tr>
<tr>
<td>call sample</td>
<td></td>
</tr>
<tr>
<td>enddo</td>
<td></td>
</tr>
<tr>
<td>end</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 9.1. Basic Grand-Canonical Ensemble Simulation. *ndisp* and *nexc* are average attempts to displace particles and to exchange particles with the reservoir, respectively; *npart* is the total number of particles; *move*, *exc*, and *sample* are subroutines\(^{55}\) (see also Appendix 1).

### 9.A.2 Histogram-Reweighting Method

#### 9.A.2.1 One-Component Systems

Histogram reweighting\(^{52,54}\) is the second component in the current simulation procedure. It rests on the observation that histograms of observables accumulated at one set of model parameters (in this case \(\beta\) and \(\mu\)) can provide estimates of histograms for other values of these parameters. Consider the frequency of occurrence \(f(N,E)\) of \(N\) particles with total configurational energy \(E\). It is given by\(^{56}\)

\[
f(N,E) = \Omega(N,V,E)e^{\frac{\beta(N-E)}{N}} / \Xi(\mu,V,T),
\]  
(9.3)
where \( \Omega(N,V,E) \) is the microcanonical partition function, \( \beta = 1/k_B T \), with \( k_B \) Boltzmann's constant, and \( \Xi \) is the grand canonical partition function. Given the distribution \( f(N,E) \) obtained in one histogram form from the simulation, the ratio of microcanonical partition functions with different values of \( N \) in the range covered by the simulation is determined from

\[
\frac{\Omega_1(N_1,V,E_1)}{\Omega_2(N_2,V,E_2)} = \frac{f(N_1,E_1)}{f(N_2,E_2)} e^{\beta [\mu (N_1 - N_2) - (E_1 - E_2)]}
\]

(9.4)

A simulation at different values \( \mu \) and \( T \) of the chemical potential and temperature, respectively, would result in a new distribution \( f'(N,E) \) with

\[
\frac{f'(N,E)}{f(N,E)} \propto e^{(\beta' \mu' - \beta \mu)N - (\beta' - \beta)E}
\]

(9.5)

Since the original simulation provides statistically significant results only over a finite range of particle number and energy, several runs need to be performed at different values of the chemical potential that result in overlapping distribution functions \( f(N,E) \).

From Eq. (9.3), the microcanonical partition function over the range of densities covered in each individual run, of index \( n \), can be obtained from

\[
\ln \Omega_n(N,V,E) = \ln[f(N,E)] - \beta \mu N + \beta E + C_n,
\]

(9.6)

where \( C_n \) is a run-specific constant equal to the logarithm of the grand partition function for the chemical potential and temperature of run \( n \).

Fig. 9.2 illustrates the histograms of two runs at different chemical potentials. There is a range of \( N \) over which the two runs overlap. Fig. 9.3 shows the raw curves for \( \mu_1 \) and \( \mu_2 \), as well as the composite curve obtained by shifting the data from the two runs by the
amount indicated by arrows, as explained below. The composite curve provides information over the combined range of particle numbers \( N \) covered by the two runs.

Simulation data are subject to statistical uncertainties, which are particularly pronounced near the extremes of particle number and energies visited during a run. When data from multiple runs are combined as shown in Fig. 9.3, the question arises of how to determine the optimal amount by which to shift the raw data in order to obtain a global free-energy function. Ferrenberg and Swendsen\textsuperscript{53} provided a solution to this problem by minimizing the differences between predicted and observed histograms. The probability distribution \( P(N, E; \mu, \beta) \) obtained from combining \( R \) runs, assumed to have the same statistical efficiency, is

\[
P(N, E; \mu, \beta) = \frac{\sum_{m=1}^{R} f_m(N, E) \exp[-\beta E + \beta \mu N]}{\sum_{m=1}^{R} K_m \exp[-\beta E + \beta \mu N - C_m]}, \tag{9.7}
\]

with \( K_m \) the total number of observations for run \( m \). The constant \( C_m \) are obtained from an iterative relationship

\[
\exp(C_m) = \sum_N \sum_E P(N, E; \mu, \beta) \tag{9.8}
\]

Given an initial guess for the set of weights \( C_m \), Eqs. (9.7) and (9.8) can be iterated until convergence is achieved. When many histograms are to be combined, this convergence of the Ferrenberg-Swendsen weights can take a long time. Once this has been achieved, all thermodynamic quantities for the system over the range of densities covered by the histograms can be obtained.
Fig. 9.2. The probability distribution \( f(N) \) for the two runs for one-component system curves for identical \( V \) and \( T \), but different \( \mu_1 \) and \( \mu_2 \) (ref. 57).

Fig. 9.3. The function \( \ln[f(N)] - \beta \mu N \) for the data of Fig. 9.2 showing the raw curves for \( \mu_1 \) and \( \mu_2 \) as well as the composite curve.
9.4.2.2 Multi-Component Systems

The histogram-reweighting methodology for multicomponent systems\textsuperscript{48-60} closely follows the one-component version described above. The probability distribution function for observing $N_1$ particles of component 1 and $N_2$ of component 2 with configurational energy in the vicinity of $E$ for a GCMC simulation at imposed chemical potential $\mu_1$ and $\mu_2$, respectively, at inverse temperature $\beta$ in a box of volume $V$, is

$$f(N_1, N_2, E) = \frac{\Omega(N_1, N_2, V, E) \exp(-\beta E + \beta \mu_1 N_1 + \beta \mu_2 N_2)}{\Xi(\mu_1, \mu_2, V, \beta)}$$  \hspace{1cm} (9.9)

Eq. (9.6) can be similarly extended to multi-component systems.

9.4.3 Mixed-Field Finite-Size Scaling

The mixed-field finite-size scaling method has proved to be the most efficient method for determining critical parameters for fluids lacking special symmetries. As a critical point is approached, the correlation length grows without bound and eventually exceeds the linear system size $L$ of the simulation box. Singularities and discontinuities that characterize the critical behavior at the thermodynamic limit are smeared out and shifted in finite systems such as those used in computer simulations. The infinite-volume critical point of a system can be extracted by examining the size dependence of thermodynamic observables with finite-size scaling theory.

The finite-size scaling computer simulation method\textsuperscript{48} involves performing a series of grand canonical simulations near the expected critical point. The resulting histograms are combined according to Eqs. (9.7) and (9.8) to obtain self-consistent estimates of the probability distributions $P(N, E; \mu, \beta)$. For one-component systems, the ordering
operator $M$ is defined as a linear combination of the number of particles $N$ and the total configurational energy $E$:

$$M \propto N - sE,$$  \hspace{1cm} (9.10)

where $s$ is the field-mixing parameter controlling the strength of the coupling between energy density fluctuations near the critical point. For multi-component systems, an extra field-mixing parameter appears for each added component, for example for binary systems,

$$M \propto N_1 - sE - uN_2,$$  \hspace{1cm} (9.11)

where $u$ is the field-mixing parameter for the number of particles of component 2.

At the critical point, the normalized probability distribution $P_L(x)$ for a given system size $L = V^{1/3}$, assumes a universal shape, with $x = A(M - M_c)$. The order parameter distribution for the three-dimensional Ising universality class is shown in Fig. 9.5. Also shown in Fig. 9.5 are the data for a colloid-polymer mixture (colloidal diameter $\sigma = 7.071$ and polymer chain length $n = 100$). The nonuniversal constant $A$ and the critical value $M_c$ of the ordering operator are chosen so that the data have zero mean and unit variance. Due to the finite-size corrections to scaling, the apparent critical temperature $T_c(L)$ and critical density $\rho_{\text{crit}}(L)$ deviate from their infinite-system values $T_c(\infty)$ and $\rho_{\text{crit}}(\infty)$. They are expected to follow scaling relationships with respect to the simulated system size, $L$:

$$T_{\text{crit}}(L) - T_{\text{crit}}(\infty) \propto L^{(\theta + 1)/\nu}$$

$$\rho_{\text{crit}}(L) - \rho_{\text{crit}}(\infty) \propto L^{(\gamma - \delta)/\nu},$$  \hspace{1cm} (9.12)

where $\theta$, $\nu$ and $\alpha$ are, respectively, the correction-to-scaling exponent, the correlation length exponent and the exponent associated with the heat capacity divergence.
Fig. 9.5. The ordering operator distribution for the three-dimensional Ising universality class (continuous line – data courtesy of N. B. Wilding). Points are the current simulation data for a colloid-polymer mixture (colloidal diameter $\sigma = 7.071$ and polymer chain length $n = 100$) on a 60x60x60 simple cubic lattice of coordination number $z = 26$. The nonuniversal constant $A$ and the critical value of the ordering operator $M_c$ were chosen so that the data have zero mean and unit variance.

9.8 Models and Simulation Details

The model underlying this work is illustrated schematically in Fig. 9.6. The colloids are modeled as hard spheres and the polymer molecules as chains of hard-sphere monomers. The size of a monomer is taken equal to one unit of the lattice. The simulations are performed on a cubic lattice of coordination number $z = 26$ to imitate
more closely the behavior in the continuum as well as to enable more flexibility for the polymer molecules. There are no attractions in the bare Hamiltonian; the polymer-polymer interaction occurs due to volume exclusion of polymer segments. The depletion interaction between colloidal particles results from depletion of polymer molecules from the regions between colloid particles as they come sufficiently close to each other.

Fig. 9.6. Schematic illustration of the model of a colloid-polymer on a lattice. A two-dimensional system is shown for simplicity, even though all calculations are performed for three-dimensional systems. The large open circles represent colloid particles, and the smaller ones represent monomers.

All simulations are performed for two box sizes: 60x60x60 for the colloidal diameters of 12.728, 7.071, and 4.243, and 20x20x20 for the colloid diameter of 1.731. Typically, after some preliminary runs (by tuning the chemical potentials of colloid ($\mu_c$) and polymer ($\mu_p$)), the values of $\mu_c$ and $\mu_p$ at which the probability distribution $P_L(N)$
exhibits a double peak structure is chosen. A long run is then carried out at these near-coexistence \( \mu_c \) and \( \mu_p \) values, in which the histogram of \( P_L(N) \) is accumulated. A histogram extrapolation based on these data is then used to extrapolate along the coexistence curve using the equal peak-weight criterion for \( P_L(N) \). In this way sizable portion of the near-critical coexistence curve can be located. Representative forms of the density distribution along the coexistence line are shown in Fig. 9.7. The number of Monte Carlo steps per run typically lies between 1 and \( 20 \times 10^9 \). The execution time required for a given number of steps is an increasing function of chain length.

Data from histograms for a given chain length and colloidal size are combined using the Ferrenberg-Swendsen algorithm,\(^{53}\) and analyzed to determine the critical point by matching the universal order parameter distribution (see Fig. 9.5). The present simulation and Ising data agree very well. Coexistence away from the critical point is obtained by determining the values of \( \mu_c \) and \( \mu_p \) that result in equal areas of vapor-like and liquid peaks. Fig. 9.8 shows the density distribution as a function of the number of particle for phase coexistence of a polymer-colloid mixture having colloidal diameter of 7.071 and polymer chain length of 250. The observed asymmetry in polymer results from the lack of symmetry between the coexisting phases.

Statistical uncertainties for critical parameters are produced from 6 to 20 independent runs, depending on the system details (colloidal size and polymer chain length), at near critical conditions with different seeds for the random number generator.
Fig. 9.7. The probability distribution of the colloid component $P_L(N_c)$ for various values of chemical potentials of colloid ($\mu_p$) and polymer ($\mu_c$) along the coexistence curve for $\sigma = 7.071$, $n = 250$, and the box length $L = 60$. $\tau$ is thermal transform and given by $\tau = -1/\mu_p$. The symbol * represents the critical condition.
Fig. 9.8. Density distribution as a function of the number of particle corresponding to phase coexistence of a polymer-colloid mixture for $\sigma = 7.071$ and $n = 250$. $N_e$ is the number of colloidal particles, and $N_p$, the number of polymer molecules.
Chapter 10: Results and Discussion

10.1 Validation of the Codes

The validity of the programs and analysis tools is first tested by comparing the simulation results for the case of a single polymer component with those of Dickman and Hall\textsuperscript{61} and with the predictions of the Flory and Flory-Huggins theories\textsuperscript{62} (see Fig. 10.1). Negligible deviation is found at low polymer concentration. For the case of pure colloid, the results for hard spheres on a lattice are compared with the prediction of the Speedy equation of state\textsuperscript{63} in the continuum (see also Fig. 10.2). In Fig. 10.2, the first solid line corresponds to the fluid phase, and second one corresponds to the crystal. The present simulation data are consistent with those of these works for colloidal reduced density up to 0.86 (amorphous close-pack reduced density).\textsuperscript{63} Significant deviation is observed for colloidal reduced density greater than 0.86 (crystal or solid phase). The discontinuity seen in our data and those predicted by Speedy EOS arises from a phase transition from fluid to solid phase. It is also noted that the corresponding values of colloidal reduced density where the phase transition occurs decrease as the colloidal diameter decreases. In all cases finite-size effects are found to be negligible.
Fig. 10.1. Pressure as function of polymer concentration determined from our simulation and from the Flory and Flory-Huggins theories. $\eta_p = \frac{nN_p}{V}$, where $\eta_p$ represents volume fraction of polymer, $n$ the number of monomers in a polymer chain, $N_p$ the number of polymer chains, and $V$ the volume of the simulation box.
Fig. 10.2. Pressure as function of polymer concentration determined from our simulation and from the Flory and Flory-Huggins theories. \( \eta_P = \frac{nN_P}{V} \), where \( \eta_P \) represents volume fraction of polymer, \( n \) the number of monomers in a polymer chain, \( N_P \) the number of polymer chains, and \( V \) the volume of the simulation box.
10.2 Dependence of Phase Diagrams on Polymer-to-Colloid Size Ratio

Two factors affect the phase diagram: the polymer-to-colloid size ratio, \( q \), and the colloid-to-monomer size ratio, which is equal to the colloidal diameter \( \sigma \) (since the size of a monomer is equal to one lattice unit). The effect of \( q \) on the phase diagrams is investigated by varying the polymer chain length and fixing the colloidal diameter, and vice versa. Figs. 10.3-10.6 illustrate various phase diagrams and snapshots of coexisting phase: liquid-liquid, solid-liquid, and three coexisting phases (gas-like liquid, liquid, and solid-like liquid). While for solid-liquid coexistence, no critical point of course exists, there is a critical point for each liquid-liquid coexistence. Figs. 10.7-10.10 show phase coexistence for various polymer chain lengths, \( n \), from 40 to 350 and a fixed colloidal diameter. The colloidal diameters corresponding to these figures are fixed at the values of 1.731, 4.243, 7.071, and 12.728, respectively. As seen from these figures, the nature of the phase coexistence changes as the colloidal diameter varies. The dependence of the nature of the phase coexistence on \( q \) and \( \sigma \) is summarized in Table 10.1. For the colloidal diameter \( \sigma = 1.731 \) and polymer chain lengths longer than 50 (\( n = 80, 120, \) and 200) (also see Fig. 10.7), only liquid-liquid coexistence is observed.

For \( n = 50 \) (\( q = 4.93 \)), both liquid-liquid and solid-liquid coexistences occur. For \( n = 30 \) (or \( q = 3.59 \)), only liquid-solid coexistence takes place. As the colloidal diameters increase (\( \sigma = 4.243 \) and \( 7.071 \)) (see Figs. 10.8 and 10.9), the range of \( n \) for which liquid-liquid coexistence is observed extends. For instance, for \( \sigma = 7.071 \) this range starts from \( n = 350 \) (\( q = 3.76 \)) to \( n = 24 \) (\( q = 0.90 \)), and for \( n = 10 \) (\( q = 0.52 \)), only solid-liquid coexistence occurs (see Table 10.1 and Fig. 10.9). In order to verify that this difference
not due to the size effect, simulations for $\sigma = 1.731$ and $n = 50$ are performed for the larger box size of 30x30x30. No difference in phase coexistence curves for the box size of 20x20x20 and 30x30x30 is observed.

It is interesting to point out that the threshold values of $q$ at which liquid-liquid coexistence disappears are larger than 0.33, in contrast to what was predicted by the mean-field theory and other approximate theories.\textsuperscript{24,28,64} For example, the present results show that liquid-liquid coexistence disappears for much larger values of $q$ ($q = 3.59$ for $\sigma = 1.731$ and $q = 0.9$ for $\sigma = 7.701$). The discrepancy between the present simulation data and the prediction from those theories described in Refs. 24, 28 and 64 is attributed to the fact that in these theories polymers are assumed to interpenetrate each other. When the radius of gyration of polymer, $R_g$, is smaller than the colloidal radius, this assumption does not introduce large errors. However, as $R_g$ is larger than colloid radius ($q$ is large), this assumption is no longer appropriate, since the effect of excluded volume between polymer segments becomes more significant, resulting in major changes in the thermodynamic properties of the systems. The larger the value of $q$ (or the smaller the colloidal diameter for a fixed value of $n$), the stronger the excluded volume effect. This effect can be observed by noting an increase in the differences $\Delta q_{th}$ in the threshold values of $q$, $q_{th}$, predicted by the theories in Refs. 24 and 28 ($q_{th} = 0.33$) and those for the cases of $\sigma = 1.731$ and $\sigma = 7.701$ ($|\Delta q_{th}(\sigma = 1.731)| = 3.29$ and $|\Delta q_{th}(\sigma = 7.071)| = 0.6$, respectively), as the colloidal size decreases.
Table 10.1. Dependence of phase coexistences on $q$ and $\sigma$. L-L represents liquid-liquid coexistence, and L-S is for liquid-solid coexistence.

<table>
<thead>
<tr>
<th></th>
<th>Only L-L</th>
<th>L-L and L-S</th>
<th>Only L-S</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma = 1.731$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n$</td>
<td>$&gt; 50$</td>
<td>$\leq 50$</td>
<td>$\leq 30$</td>
</tr>
<tr>
<td>$q$</td>
<td>$&gt; 4.93$</td>
<td>$\leq 4.93$</td>
<td>$\leq 3.59$</td>
</tr>
<tr>
<td>$\sigma = 7.071$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n$</td>
<td>$\geq 24$</td>
<td>-</td>
<td>$\leq 10$</td>
</tr>
<tr>
<td>$q$</td>
<td>$\geq 0.90$</td>
<td>-</td>
<td>$\leq 0.52$</td>
</tr>
</tbody>
</table>
Fig. 10.3  Solid-liquid phase coexistence: There is of course no critical point in this case. $\eta_p$ is defined as in Fig. 10.1. The dashed lines are tie lines.
Fig. 10.4. Solid-liquid and liquid-liquid coexistence: There is a critical point (the isolated middle point) for liquid-liquid coexistence. The solid line connects the points of the solid phase and those of the liquid phase. The dashed line connects coexisting colloid-rich and colloid-lean liquid phases.
Fig. 10.5. Liquid-liquid coexistence: The critical point is indicated by the arrow.
Fig. 10.6. One snapshot of coexisting phases: solid-liquid (a), liquid-liquid viewed from an arbitrary angle (b) and from the side (c)
Fig. 10.7. Phase coexistence of the polymer-colloid system for $\sigma = 1.731$ and $n = 30$ to 200.
Fig. 10.8. Liquid-liquid phase diagram of the polymer-colloid system with $\sigma = 4.243$ and $n = 60$ to 350.
Fig. 10.9. Liquid-liquid phase coexistence of the polymer-colloid system with $\sigma = 7.071$ and $n = 60$ to 350.
Fig. 10.10. Liquid-liquid phase coexistence of the polymer-colloid system with

\[ \sigma = 12.728 \text{ and } n = 60 \text{ to } 250. \]
It is also observed from Figs. 10.7-10.10 that the critical colloidal and polymer volume fractions decrease as the polymer chain length increases ($q$ increases). For various $q$ ratios, the critical colloidal volume fractions tend, by extrapolation, to approach finite values. This trend is qualitatively consistent with that observed in the study of Bolhuis et al.\textsuperscript{42} for interacting polymer and hard-sphere colloids, even though there is a quantitative discrepancy in the values of the critical parameters (see Figs. 10.11-10.13, where the volume fraction of polymer is defined by $\Phi_p = \rho_p \frac{4}{3} \pi R^3$, with $\rho_p$ being the number density of the polymer). For instance for $q = 3.92$ (Fig. 10.12), the present estimated colloid and polymer critical parameters are $\Phi_c = 0.128$ and $\Phi_p = 0.829$, whereas those values interpolated from Bolhuis et al.'s work are $\Phi_c \approx 0.24$ and $\Phi_p \approx 1.9$, respectively. These differences can be attributed to the fact that a larger coordination number ($z = 26$) is used here, which is expected to be more realistic because it better approximate the continuum than that used in Bolhui et al.'s study ($z = 6$). Furthermore, the critical parameters depend not only on the polymer-to-colloid size ratio $q$ but also on the colloidal diameter. The effect of colloidal diameter on the critical parameters can be seen, for example, by comparing the critical colloid and polymer parameters at the same value of $q = 2.38$ for the cases of $\sigma = 4.243$ and $n = 60$ and of $\sigma = 7.071$ and $n = 150$ (see Figs. 10.8-10.9). The critical colloidal reduced density and polymer volume fractions are $\rho \sigma^3 = 0.26$ and $\eta_p = 0.068$ for the former, and $\rho \sigma^3 = 0.326$ and $\eta_p = 0.042$ for the latter.
Fig. 10.11. For comparing with Bolhuis et al.'s work, the data from Fig. 10.9 are plotted with $\Phi_p = \rho_p \frac{4}{3} \pi R_g^3$ and $\Phi_c = \rho_c \frac{4}{3} \pi \sigma^3$, where $\rho_p$ and $\rho_c$ are polymer and colloid densities, respectively.
Fig. 10.12. For comparing with Bolhuis et al’s work, the data from Fig. 10.8 are plotted. \( \Phi_c \) and \( \Phi_p \) are defined as those in Fig. 10.11.

Fig. 10.13. Simulation data reproduced from Ref. 42 (Bolhuis et al’s work); \( \Phi_c \) and \( \Phi_p \) are defined as those in Fig. 10.11.
The present results of critical volume fractions of colloid and polymer are also compared with those by Sear\textsuperscript{39} in his analytical study of Flory-Huggins theory for athermal mixtures of hard spheres and large flexible polymer. In Sear's study, the monomer size $a$ is rescaled to $\sigma$ (colloidal diameter) by viewing the polymer as a chain of $n_B$ monomers of size $\sigma$. The critical density of monomer, which is also equal, in this case, to the critical polymer volume fraction $\eta_p$, is found to decrease as $1/\sqrt{n_B}$, and the density of spheres tends to a constant $\sim 1/(8b)$, where $b$ is a parameter measuring the quality of the solvent (Sear takes $b = 3.9$ for good solvent). In Table 10.2, the polymer and colloidal volume fractions are compared with those determined from Sear's theory. As seen from Table 10.2 (where the critical parameters are determined with $n_B = n$, and $b = 3.9$), the trend is qualitatively the same as that of the present simulation results; i.e., the polymer and colloidal volume fractions decrease with increasing polymer chain length. However, quantitatively large deviations between our data and those predicted by Sear's theory occur.
Table 10.2. Critical parameters for various values of $\sigma$ and $n$ are compared with those predicted by Sear’s theory.\textsuperscript{39} $\eta_p^*$ and $\rho_c^* \sigma^3$ are the critical polymer and colloidal reduced density, respectively. The calculations of critical parameters using Sear’s theory are performed with $n_B = n$, and $b = 3.9$.

<table>
<thead>
<tr>
<th>$\sigma$</th>
<th>$n_B = n$</th>
<th>$\eta_p^*$</th>
<th>$\rho^* \sigma^3$</th>
<th>$\eta_p^*$ (Ref. 39)</th>
<th>$\rho^* \sigma^3$ (Ref. 39)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.728</td>
<td>150</td>
<td>0.029</td>
<td>0.471</td>
<td>0.037</td>
<td>0.075</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>0.025</td>
<td>0.335</td>
<td>0.029</td>
<td>0.072</td>
</tr>
<tr>
<td>7.071</td>
<td>150</td>
<td>0.042</td>
<td>0.326</td>
<td>0.037</td>
<td>0.075</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>0.036</td>
<td>0.315</td>
<td>0.029</td>
<td>0.072</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>0.033</td>
<td>0.310</td>
<td>0.024</td>
<td>0.070</td>
</tr>
<tr>
<td>4.243</td>
<td>150</td>
<td>0.052</td>
<td>0.245</td>
<td>0.037</td>
<td>0.075</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>0.045</td>
<td>0.238</td>
<td>0.029</td>
<td>0.072</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>0.040</td>
<td>0.238</td>
<td>0.024</td>
<td>0.070</td>
</tr>
<tr>
<td>1.732</td>
<td>120</td>
<td>0.119</td>
<td>0.340</td>
<td>0.041</td>
<td>0.076</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>0.107</td>
<td>0.328</td>
<td>0.032</td>
<td>0.073</td>
</tr>
</tbody>
</table>
The effect of the polymer-to-colloid size ratio is also examined by varying the colloid size and fixing the polymer chain length. Fig. 10.14 illustrates the phase transitions of the colloid-polymer system for \( n = 150 \) and \( \sigma = 4.243, 7.071, \) and \( 12.728. \) As the colloidal size decreases, the critical colloidal volume fraction decreases, and the critical polymer volume fraction increases. The same observation applies when the polymer chain length \( n \) is fixed at 60, 100, 150, and 350 (the phase diagrams for these cases are not shown). For a fixed polymer chain length, as the colloidal diameter further decreases, the attractive potential becomes weaker and longer in range. Consequently, more polymers are required to induce the phase transition and the resulting lower colloidal volume fraction.

It is interesting to note that the trend of the critical polymer volume fraction \( \eta_p \) \((\eta_p = \frac{nN_p}{V})\) increasing with increasing values of \( q \), which is observed in Fig. 10.14, contrasts with that observed in Figs. 10.7-10.10, where the colloidal diameter is fixed, and the polymer chain length is varied. The contradiction stems from the fact that details of the polymer-polymer interaction in these cases differ. In both cases, the depletion forces are weakened by either decreasing the colloidal diameter for a fixed polymer chain length or by increasing the polymer chain length for a fixed colloidal diameter. In the former case, the polymer-polymer interactions themselves are unchanged, requiring a higher polymer volume fraction in order to induce phase separation. In the latter case, on the other hand, the polymer-polymer interactions themselves increase due to an increase in polymer size, which facilitates phase separation. Therefore, the requirement of increasing the polymer volume fraction in order to induce phase separation due to the decrease of the depletion force is not necessary in this case.
Fig. 10.14. Phase diagram for a colloid-polymer system with $n = 150$ and $\sigma = 4.243$ to 12.728. $\eta_p = \frac{nN_p}{V}$. 
Fig. 10.15 shows another way of plotting the data of Fig. 10.14. Noteworthy from this figure is that the polymer volume fraction \( \Phi_p \), defined as \( \rho_p \frac{4}{3} \pi R_g^3 \), increases with decreasing colloidal diameter, consistent with what is observed in Figs. 10.11 and 10.12, where the same variable \( \Phi_p \) instead of \( \eta_p \) is used. In other words, \( \Phi_p \) increases as \( q \) increases either by increasing \( n \) and fixing \( \sigma \) or vice versa. This behavior differs from that observed from Figs. 10.7-10.10 and 10.14, where opposite trends are observed when the variable \( \eta_p \) is used (see the previous paragraph). This discrepancy is explained by the fact that \( R_g \) depends on the polymer concentration and the polymer chain length, and that the polymer molecules are assumed to be spherical. As the polymers become very large, the assumption of sphericity is no longer appropriate due to significant entanglement of the polymer chains. Furthermore, in the semi-dilute regime, the only relevant scale is the correlation length \( \xi \), given by \( \xi = a(c/a)^{3/4} \), where \( a \) is the monomer size, and \( c \) is the polymer concentration as defined in Ref. 33. The radius of gyration is not a relevant length scale as it is much larger than \( \xi \), and the chain then loses its correlations. On the other hand, the variable \( \eta_p \), more accurately representing the monomer fraction in this case, does not depend on any regimes and the polymer shape. The use of the variable \( \eta_p \), therefore, seems to be more appropriate to distinguish the subtle difference in the polymer-polymer interaction as explained in the previous paragraph.
Fig. 10.15. Phase diagram for a colloid-polymer system with \( n = 150 \) and \( \sigma = 4.243 \) to 12.728. \( \Phi_p = \rho_p \frac{4}{3} \pi R^3 \).
10.3 Scaling of Critical Parameters with Polymer Chain Length

and “Protein Limit”

As noted above, for a fixed colloidal diameter, the critical polymer and colloidal volume fractions appear to approach finite values as the polymer chain length is extrapolated to infinity. To determine these limiting values, the critical parameters (colloidal and polymer volume fractions) are plotted as a function of chain length: 

\[ y_i(n) = n^{-\gamma_i} \quad (i = \text{colloid, polymer}), \]

where \( \gamma \) is the value that gives the best fit. Linear regression of the data is performed for \( n \geq 40 \) for \( \sigma = 7.071 \), \( n \geq 100 \) for \( \sigma = 4.243 \), and \( n \geq 50 \) for \( \sigma = 1.731 \). The extrapolated critical colloidal and polymer volume fractions at infinite polymer chain length are summarized in Table 10.3. The values of the exponents obtained for all cases (different values of \( \sigma \)) appear not to approach the universal value of 0.5 as predicted by the Flory-Huggins theory for the case where there is only polymer. Furthermore, the critical colloid volume fraction at infinite chain length slightly decreases as the colloidal diameter decreases. No similar trend is observed for the critical polymer volume fraction at infinite chain length as \( \sigma \) varies.

For the “protein limit,” the excluded volume interaction between polymers becomes essential especially when the polymer concentration approaches the coil overlap (semidilute regime, \( \Phi_p \sim 1 \)). According to the studies of de Gennes\(^\text{31, 32}\) and Odijk\(^\text{34-36}\), as the correlation length \( \xi \) gets larger than the colloidal radius \( R_c \), the depletion interaction becomes weaker and the onset of phase separation shifts to larger polymer concentration. While miscibility is predicted in these earlier works, the present results
indicate that miscibility does not persist at that limit. A similar conclusion was reached in a recent work by Schweizer et al.\textsuperscript{41}

Table 10.3. Scaling of critical parameters with polymer chain length. $\gamma_c$ and $\gamma_p$ represent the exponent; $\rho_c^*$, $\Phi_c^*$, and $\eta_p^*$ are the critical colloid density, critical colloidal volume fraction, and critical polymer volume fraction, where $\eta_p^* = \frac{n N_p^*}{V}$ and $\Phi_c^* = \frac{\pi}{6} \sigma^3 \rho_c^*$.

<table>
<thead>
<tr>
<th>$\sigma$</th>
<th>$\gamma_c$</th>
<th>$\gamma_p$</th>
<th>$\rho_c^* \sigma^3$</th>
<th>$\eta_p^*$</th>
<th>$\Phi_c^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.071</td>
<td>0.47+-0.02</td>
<td>0.39+-0.01</td>
<td>0.2762+-0.0007</td>
<td>0.01037+-0.00006</td>
<td>0.1446+-0.0004</td>
</tr>
<tr>
<td>4.243</td>
<td>0.91+-0.09</td>
<td>0.32+-0.02</td>
<td>0.231+-0.002</td>
<td>0.003+-0.001</td>
<td>0.121+-0.001</td>
</tr>
<tr>
<td>1.731</td>
<td>0.14</td>
<td>0.61</td>
<td>0.200+-0.012</td>
<td>0.080+-0.002</td>
<td>0.105+-0.001</td>
</tr>
</tbody>
</table>
10. 4 Suggestions for Future Work

Although several features of the phase behavior of the colloid-polymer system can be understood by using the present simple model of purely repulsive components, further insights into the thermodynamics of polymer-colloid mixtures would be gained upon adding attractive forces. This would illuminate the competition between effective attractive forces of entropic origin due to depletion and bare conventional attractive forces. Moreover, the role of the solvent is another problem worthy of investigation.
Part IV

Depletion Interaction in One Dimension:

Short-Range Order
Chapter 11: Introduction

In its simplest approximation, i.e., that of Asakura and Oosawa,\(^1\) the depletion force is evaluated for a \(d\)-dimensional system of colloidal particles and ideal polymers, in which the polymer is modeled as a sphere of radius equal to its radius of gyration, and the colloid-polymer interaction is assumed to be that of hard spheres. The depletion force is found to be proportional to the \((d-1)\)-dimensional volume of the projection, on the plane perpendicular to the line joining the centers of two neighboring spherical particles, of the intersection of the excluded volumes of these particles. Therefore, for one-dimensional systems the intersection reduces to a point, independent of the colloid particle separation provided that their centers are close enough that no polymer can fit between them. Consequently, the depletion force is thus constant and the depletion potential, equal up to the sign, to the integral of the depletion force, is a linear function of the separation between neighboring particles of the type studied here and in another recent study.\(^2\)

One-dimensional continuous systems of hard rods with (or without) nearest-neighbor attractive interactions have been investigated for a long time.\(^3\)\(^-\)\(^9\) The main importance of these systems lies in the fact that in contrast to two- or three-dimensional continuous systems, exact analytic results can be obtained for most quantities of interest, in
particular, correlation functions.\textsuperscript{10-16} Moreover, such one-dimensional systems provide valuable insight into the complex static and dynamic properties of higher dimensional systems, and enable approximate methods to be tested and developed for the latter.\textsuperscript{17-19} Particularly illuminating illustrations of this role played by linear systems are the manifold pioneering investigations of Percus,\textsuperscript{20-22} the study of Fisher and Widom,\textsuperscript{23} of the long-range behavior of the pair correlation function, and the recent analysis of Lekkerkerker and Widom\textsuperscript{24} of the depletion interaction in hard sphere mixtures.

Lattice systems are well-known to be much more amenable to exact analytic analysis than their continuous analogues. However, an extended hard core is needed in lattice systems to propagate the effect of the repulsive part of the potential on the correlation functions,\textsuperscript{25} and this then makes the theoretical analysis no simpler than that for systems in the continuum.\textsuperscript{23}

In this work, a system of one-dimensional hard rods in the continuum interacting with nearest-neighbor potential is considered. While exact expressions of the pair correlation function for these systems (and hence, since the Kirkwood superposition approximation is exact for these models, for all n-body correlation functions) were derived fifty years ago by Salsburg \textit{et al.},\textsuperscript{26} it has apparently not been noted that the short-range behavior of the pair correlation function can be expressed analytically in simple form. This form is derived and used in this work to derive the exact analytic expression of the pair correlation function at short distances for the linear potential. As explained above, this potential is related to the depletion interaction in linear systems.\textsuperscript{27}
Chapter 12: Pair Correlation Function: Derivations and Results

12.1 Derivation

Consider a system of $N$ identical particles of length (diameter) $a$, located at the points $R_1, ..., R_N$ on a line of length $L$. Assuming that the potential energy $\Phi_N$ is the sum of pair potentials between nearest-neighboring particles, and choosing

$$0 < R_1 < R_2 < ... < R_N < L,$$

we have

$$\Phi_N = \sum_{i<j} \Phi(R_{ij}) = \sum_{j=1}^{N-1} \Phi(R_{j+1} - R_j),$$

(12.1)

where $\Phi(R)$ is the interaction potential between nearest-neighbor particles $j$ and $j+1$ respectively located at $R_j$ and $R_{j+1}$.

If one assumes that the walls act as particles identical with those of the system, fixed at $R = 0$ and $R = L$, the total potential energy becomes

$$\Phi_N = \Phi(R_1) + \sum_{j=1}^{N-1} \Phi(R_{j+1} - R_j) + \Phi(L - R_N).$$

(12.2)

$\Phi(R)$ is further assumed to satisfy:

(a) $\lim_{R \to 0} \Phi(R) = \infty$
(b) \( \lim_{R \to \infty} \Phi(R) = 0 \).

The average number density, i.e., the probability per unit length that any molecule will be at the point \( r \), is defined as,\(^{26}\)

\[
\rho^{(1)}(r) = \sum_{k=1}^{N} \left \langle \delta(R_k - r) \right \rangle_{Av} = \left \langle \sum_{k=1}^{N} \delta(R_k - r) \right \rangle_{Av} .
\] (12.3)

Similarly, the average density of ordered pairs is given by\(^{26}\)

\[
\rho^{(2)}(r, r') = \left \langle \sum_{k=1}^{N} \sum_{j=\neq k}^{N} \delta(R_k - r) \delta(R_j - r') \right \rangle_{Av} ;
\] (12.4)

here \( \rho^{(2)} \) is the probability per (unit length\(^2\)) that one molecule will be at \( r \) and another will be at \( r' \). For hard-core models with a hard-core diameter (length) \( a \) and an attraction of range \( \lambda \), the interaction potential takes the form:

\[
\Phi(R) = \begin{cases} 
\infty & R < a \\
\Phi(R) & a \leq R \leq \lambda \\
0 & R > \lambda .
\end{cases}
\] (12.5)

If \( r \) and \( r' \) are allowed to become infinite in such a manner that \( r-r' \) remains fixed (thermodynamic limit), the following expressions are obtained:\(^{26}\)

\[
\rho^{(1)} = 1/la ; \quad l = L / [(N+1)a] ,
\] (12.6a)

\[
\rho^{(2)}(R) = \sum_{n=1}^{N-1} \frac{A(R - na)}{la} \frac{1}{2\pi i} \int_{c-\infty i}^{c+\infty i} ds \left[ \frac{\Omega(s)}{\Omega(c)} \right]^n \exp \left[ - R(s - c) \right] ,
\] (12.6b)

\[
\rho^{(2)}(R) = \rho^{(2)}(-R).
\]

where \( R = r - r' \), and \( A \) is the step function:
\[ A(x) = \begin{cases} 
0 & x < 0 \\
1 & x \geq 0 
\end{cases}, \quad (12.7) \]

\[ \Omega(s) \text{ is the Laplace transform} \]

\[ \Omega(s) = \int_0^\infty dR \exp \left[-sR - \beta \Phi(R)\right] = \mathcal{L}\left[ e^{-\beta \Phi(R)} \right], \quad (12.8) \]

and \( c \) by solving the stationary condition for the saddle point:\footnote{26}

\[ \left( \frac{\partial f}{\partial s} \right)_{s = c} = 0, \quad (12.9a) \]

where

\[ f(s) = \frac{Ls}{N+1} + \ln \Omega(s). \quad (12.9b) \]

For a system of rigid spheres (rods) with no attraction, one readily finds \( c = 1/[a(l-1)] \).

Consider next the short-range behavior, i.e. \( n = 1 \) and \( n = 2 \), where \( 0 \leq R \leq 3a \).

For \( n = 1 \), the first term of the sum in Eq. (6b) can be rewritten as\footnote{27}

\[ T_1(R) = \frac{A(R-a)}{la} \frac{1}{2\pi i} \int_{c+\infty i}^{c-\infty i} ds \ e^{Rs} \Omega(s) \frac{e^{-Rc}}{\Omega(c)} \]

\[ = \frac{A(R-a)}{la} \mathcal{L}^{-1}\left[ \mathcal{L}\left[ e^{-\beta \Phi(R)} \right] \right] \frac{e^{-Rc}}{\Omega(c)} \]

\[ = \frac{A(R-a)}{la} \frac{e^{-Rc}}{\Omega(c)} e^{-\beta \Phi(R)} \]

\[ = \frac{A(R-a)}{la} \frac{e^{-Rc}}{\Omega(c)} I_1(R), \quad (12.10a) \]

where
\[ I_1(R) = e^{-\beta \Phi(R)}. \] (12.10b)

Let
\[ I_n(R) = \frac{1}{2\pi i} \int_{c - i \infty}^{c + i \infty} ds \ e^{R \cdot s} \left[ \mathcal{L}(s) \right]^n, \] (12.11)

so that
\[ I_2(R) = \frac{1}{2\pi i} \int_{c - i \infty}^{c + i \infty} ds \ e^{R \cdot s} \left[ \mathcal{L}(s) \right]^2. \] (12.12)

This multiple integral is evaluated by using the relation,
\[ \int_0^\infty e^{-s^t} f_{(m)}(t) \ dt = \left[ \int_0^\infty e^{-s^t} f(t) \ dt \right]^m, \] (12.13)

where
\[ f_{(N+1)}(u) = \int_0^u dx_N \int_0^{x_N} dx_{N-1} \ldots \int_0^{x_2} f(u-x_N) f_{N,N-1} \ldots f_{2,1} f(x_1) \ dx_1, \] (12.14)

with
\[ f_{N,N-1} = f(x_N - x_{N-1}) \]

and
\[ f(u,v) = e^{-\beta \Phi(|u-v|)}. \] (12.15b)

The integral in Eq. (12.12) then reads
\[ I_2(R) = \frac{1}{2i\pi} \int_{c - i \infty}^{c + i \infty} ds \ e^{R \cdot s} \left[ \int_0^\infty dR \ e^{-s \cdot R} e^{-\beta \Phi(R)} \right]^2 \]
\[ = \frac{1}{2i\pi} \int_{c - i \infty}^{c + i \infty} ds \ e^{R \cdot s} \left[ \int_0^\infty dR \ e^{-s \cdot R} f_{(2)}(R) \right] \]
\[ = \int_0^R dR' \exp \left\{ -\beta \left[ \Phi(R-R') + \Phi(R') \right] \right\}, \] (12.16)

and the second term in Eq.(12.6b) thus becomes
\[ T_2(R) = \frac{A(R-2a)}{la} \frac{e^{-R'}}{[\Omega(c)]^2} \int_0^R dR' \exp \left\{ -\beta \left[ \Phi(R-R') + \Phi(R') \right] \right\} \]

\[ = \frac{A(R-2a)}{la} \frac{e^{R'}}{[\Omega(c)]^2} I_2(R). \]  \hspace{1cm} (12.17)

The average density in terms of \( T_1(R) \) and \( T_2(R) \) thus has the simple forms:

\[ \rho^{(2)}(R) = T_1(R) \quad \text{for } R \leq 2a, \]  \hspace{1cm} (12.18a)

\[ \rho^{(2)}(R) = T_1(R) + T_2(R) \quad \text{for } R \leq 3a. \]  \hspace{1cm} (12.18b)

The pair correlation function is related to the average density by

\[ g^{(2)}(R) = \rho^{(2)}(R)(1/a)^2. \]  \hspace{1cm} (12.19)

We next derive the short-range behavior of the pair correlation function of the hard rod model with a linear attractive potential, which describes the depletion interaction in one dimension.

The linear potential has the form:

\[ \Phi(R) = \begin{cases} 
\left( \frac{\varepsilon}{\lambda-a} \right) x - \frac{\lambda \varepsilon}{\lambda-a} = \eta x - \xi & \text{for } a \leq x \leq \lambda \\
+\infty & \text{for } x < a \\
0 & \text{for } x > \lambda,
\end{cases} \]  \hspace{1cm} (12.20)

where

\[ \eta = \frac{\varepsilon}{\lambda-a} \quad \text{and} \quad \xi = \frac{\lambda \varepsilon}{\lambda-a}. \]

The expression of \( \Omega(s) \) then takes the form
\[ \Omega(s) = \int_a^\lambda dR \exp[-(sR + \eta R - \xi)] + \int_\lambda^\infty dR \exp(-sR) \]
\[ = \frac{\exp(\beta \xi)}{(s + \beta \eta)} \left\{ \exp[-(s + \beta \eta) a] - \exp[-(s + \beta \eta) \lambda] \right\} \]
\[ + \frac{1}{s} \exp(-\lambda s). \]  
(12.21)

The expression \( I_n(R) \) is determined as in Section 1. We obtain:

\[ I_1(R) = \exp[-\beta \Phi(R)] = \exp[-\beta (\eta R - \xi)]. \]

The first term in Eq. (6b) then becomes

\[ T(R) = \begin{cases} 
0 & R < a \\
\frac{1}{la} \frac{\exp(-Rc)}{\Omega(c)} \exp[-\beta (\eta R - \xi)] & a \leq R \leq \lambda \\
\frac{1}{la} \frac{\exp(-Rc)}{\Omega(c)} & \lambda < R.
\end{cases} \]  
(12.22)

For \( n = 2 \), we again distinguish two cases:

(i) \( \lambda = 2a \)

For \( 2a \leq R \leq 3a \),

\[ I_2(R) = \int_a^{2a} dR' \exp \left\{ -\beta \left[ (\eta R' - \xi) + \Phi(R - R') \right] \right\}. \]

Let \( x = R - R' \), and \( y + 2a = R \), with \( 0 \leq y \leq a \). One finds

\[ I_2(R) = \int_y^{a+y} dx \exp \left\{ -\beta \left[ (\eta R' - \xi) + \Phi(x) \right] \right\} \]
\[ I_2(R) = \int_a^{3a/2} dR' \exp \left\{ -\beta \left[ \eta R' - \xi + \Phi(R - R') \right] \right\}. \]

Let \( x = R - R' \)

\[ I_2(R) = \int_{R-a}^{R-3a/2} dx \exp \left\{ -\beta \left[ \eta R' - \xi + \Phi(x) \right] \right\}. \]

Let \( R = 2a + y \) with \( 0 \leq y \leq a/2 \)

\[ I_2(R) = (R - 2a) \exp \left\{ -\beta \left( \eta R - 2 \xi \right) \right\}. \] (12.24)

For \( 5a/2 \leq R \leq 3a \), \( I_2(R) \) takes the form

\[ I_2(R) = \int_a^{3a/2} dR' \exp \left\{ -\beta \left[ \eta R' - \xi + \Phi(R - R') \right] \right\} \]

\[ + \int_{3a/2}^{2a} dR' \exp \left\{ -\beta \Phi(R - R') \right\}. \]

Let \( x = R - R' \) and \( R = 5a/2 + y \), with \( 0 \leq y \leq a/2 \)

\[ I_2(R) = \int_{3a/2+y}^{a+y} (-dx) \exp \left\{ -\beta \left[ \eta R' - \xi + \Phi(x) \right] \right\} \]

\[ + \int_{a/2+y}^{a+y} (-dx) \exp \left\{ -\beta \Phi(x) \right\} \]

\[ = (3a - R) \exp \left\{ -\beta \left[ \eta R - 2 \xi \right] \right\} \]
\[
\exp \left[ \frac{\beta ( -\eta R + \xi )}{\beta \eta} \right] \left[ \exp \left[ \frac{\beta \eta ( R - a )}{3 / 2 \beta \eta a} \right] - \exp \left( \frac{3}{2} \beta \eta a \right) \right] \\
- \exp \left( \frac{\beta \xi}{\beta \eta} \right) \left[ \exp \left[ -\beta \eta ( R - \frac{3}{2} a ) \right] - \exp \left( -\beta \eta a \right) \right]. (12.25)
\]

12.2 Discussion

The exact results derived above are used here to plot the short-range behavior of the pair correlation function for different values of the parameters of the intermolecular potential and of the density (Fig. 12.1). Noteworthy of this graph is their apparently remarkable variety. Several of these features are readily accounted for: in particular, the discontinuities of the first derivative of the pair correlation functions, clearly seen for example in Fig. 12.1 are direct manifestations of those of the intermolecular potentials themselves; and for very dilute systems, i.e., for large values of the parameter \( l \), the density expansion of the pair correlation function yields a short-range behavior which by necessity directly mimics the potential, as seen in Fig. 12.1(c).

In a forthcoming paper, the present exact results for the linear potential will be compared to those of our ongoing experiments on one-dimensional colloid-polymer systems\(^{28}\) (see photograph of Fig. 12.2), and a qualitative comparison will be attempted with those of our experiments on two-dimensional colloid-polymer systems.
Fig. 12.1. Pair correlation function $g(r)$ for linear potential with various values of $\varepsilon, \lambda$, and $l$.

Fig. 12.2. Polymer-colloid system in one dimension (from Ref. 28). The solid dark circles are colloidal particles. Polymer is not visible.
12.3 Suggestions for Future Work

It would be interest to investigate the effect of the walls on the thermodynamics and correlation function of one-dimensional colloid-polymer systems, by extending the above analytical study so as to include an external field. This amounts to adding a one-body interacting potential to the Hamiltonian. Such a system should be amenable to an exact analytical treatment on a lattice using the transfer matrix method of statistical mechanics.
Appendix 1: SUBROUTINES FOR GRAND CANONICAL MONTE CARLO SIMULATION

Subroutine MOVE

<table>
<thead>
<tr>
<th>SUBROUTINE move</th>
<th>attempts to displace a particle</th>
</tr>
</thead>
<tbody>
<tr>
<td>o = int(ranf()*npart) + 1</td>
<td>select a particle at random</td>
</tr>
<tr>
<td>call ener(x(o), eno)</td>
<td>energy old configuration</td>
</tr>
<tr>
<td>xn = x(o) + (ranf()-0.5)*delx</td>
<td>give particle random displacement</td>
</tr>
<tr>
<td>call ener(xn, enn)</td>
<td>energy new configuration</td>
</tr>
<tr>
<td>if (ranf().lt.exp(-beta*(enn-eno)))</td>
<td>accepted: replace x(o) by xn</td>
</tr>
<tr>
<td>xn = xo</td>
<td>return</td>
</tr>
<tr>
<td>end</td>
<td></td>
</tr>
</tbody>
</table>

Note: xo and xn are the coordination of the old and new configurations; eno and enn is the energy of the old and new configurations; delx is displacement decrement; beta = 1/k_BT, where T.

Comments to this algorithm:

1. Subroutine ener calculates the energy of a particle at the given position.
2. If a configuration is rejected, the old configuration is retained.
3. The ranf() is a random number uniform in [0,1].
Subroutine EXC

```
SUBROUTINE exc
  if (ranf().lt.0.5) then
    if (npart.eq.0) return
    o = int(npart*ranf()) + 1
    call ener(x(o), eno)
    arg = npart*exp(beta*eno)/(zz*vol)
    if (ranf().lt.arg) then
      x(o) = x(npart)
      npart = npart - 1
    endif
  else
    xn = ranf()*box
    call ener(xn, enn)
    arg = zz*vol*exp(-beta*enn)/(npart+1)
    if (ranf().lt.arg) then
      x(npart + 1) = xn
      npart = npart + 1
    endif
  endif
return
end
```

Note: \( zz = \exp(\beta \mu)/\Lambda^3 \), where \( \Lambda \) is the de Broglie wave length.
REFERENCES

Part 1: *ab initio* on Interaction of Fe Atoms with Single-Wall carbon Nanotubes


33. CP code: Car-Parrinello variable-cell molecular dynamics, developed by A. Pasquarello (IRRMA, Lausanne), K. Laasonen (Oulu), A. Trave (UC Berkeley), R. Car (Princeton), P. Giannozzi, N. Marzari (MIT) and others, based on the original code written by R. Car and M. Parrinello.
34. The ultrasoft pseudopotential was obtained from Filippo de Angelis private communication.
Part II: Magnetic Phase Transitions and Long-Range Order of Magnetic Carbon Nanotubes


R. J. Baierle et al, Phys. Rev B 64, 85413 (2001);
18. R. S. Iskhakov et al, JETP Lett. 78, 236 (2003);
Suematsu et al., ibid 12, 377(1985) ; H. Akera and H.Kamimura, Solid State
ibid. 12, 427 (1985); I. Oyuro et al., ibid. 12, 449 (1985); G. Dresselhaus, S.T.
24. S. Nagase et al. in: Fullerenes Chemistry and Physics and Technology,
K.M.Kardish and R. S. Ruoff (Eds.), Wiley-Interscience, New York, 2000, pp-
395-429.
(2000).
26. J. Samuel Smart, Effective Field Theories of Magnetism, IBM Waston Research


Part III: Computer Simulation of Polymer-Colloid Systems in Three Dimensions


Part IV: Depletion Interaction in One Dimension: Short-Range Order

   (1953).