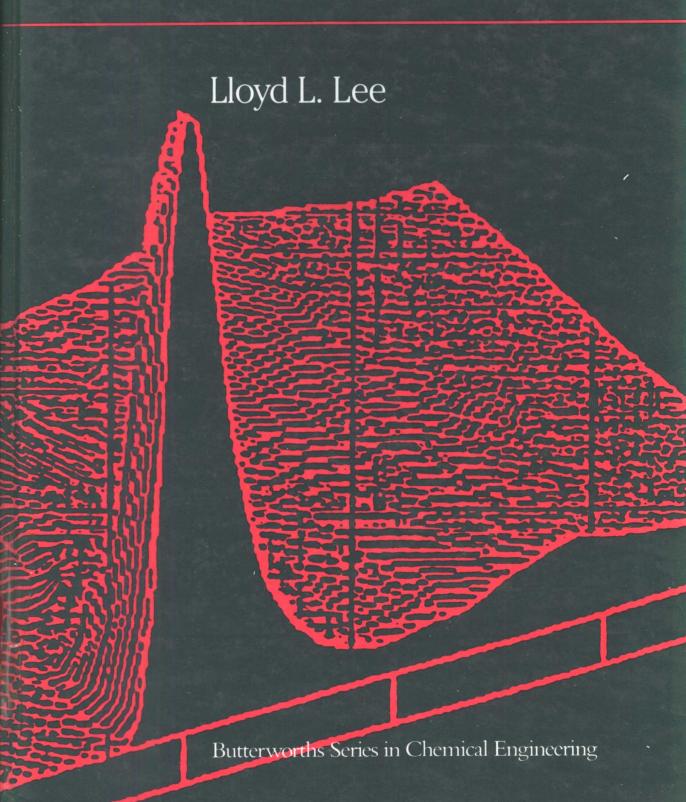# Molecular Thermodynamics of Nonideal Fluids

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MOLECULAR THERMODYNAMICS

OF NONIDEAL FLUIDS

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PREFACE

The theoretical study of the physical properties of fluids (liquids and gases) has made significant advances in the last 30 years. The progress has been due chiefly to a three-prong development in (a) molecular theories based on the methods of statistical mechanics, (b) numerical simulations of molecular movements on fast electronic computers, and (c) scattering experiments with x-ray, neutrons, and other probes. Earlier, simple physical models were used to represent spherical molecules, such as argon. Gases like these are not of interest to practicing engineers. This state of affairs persisted into the 1950s and 1960s. In the 1970s, the situation improved considerably: fluids with polar forces (water, ammonia, and alcohols) and nonspherical shapes (polyatomics and hydrocarbons) were studied. In addition, charged particles (plasmas and ionic solutions), long-chain molecules (polymer solutions), and liquid metals were investigated. Studies of these "realistic" fluids were made possible by a combination of factors: development of the probability distribution function theories in statistical mechanics (e.g., the perturbation theories) and refinement of computer simulation methods (Monte Carlo random walks and molecular dynamics solution of the equations of motion). Currently, the new methods of investigation are expanding rapidly into fluid materials such as liquid crystals, colloidal solutions, biological fluids, polyelectrolytes, amphiphilic molecules, and polydisperse systems. Diverse phenomena found in the fluid state are being examined, such as phase transition, chemical reactions, adsorption at interfaces, and transport phenomena.

These new developments have made the field of molecular theories not only interesting but also "useful" to engineers. However, due to the interdisciplinary preparation and the requisite mathematical sophistication, the new information remained inaccessible to many segments of the engineering community. The situation has improved markedly since the 1970s and the uptake continued into the 1980s, as witnessed by the increased number of courses offered in engineering colleges on molecular thermodynamics and statistical mechanics, as well as seminars held at professional meetings on molecular-based studies of fluids. At the same time, there are needs for textbooks written for an engineering audience. Books in statistical mechanics were conventionally written for theoretical physicists and chemists. Although many are definitive works in the field (see Appendix D. Bibliography), few are suited as introductions to the subject. Others were devoted to specialized fields not of interest to engineers.

With this in mind, we have written this book to address a different need, the need to bring the molecular methods to engineers. Our presentation is introductory. Thus many subjects of prime interest to researchers were eliminated. It is a difficult, or even impossible, task to keep molecular theories on an elementary level. Compromises will have to be made. We are at the same time application-minded. Whenever possible, applications of interest to chemical engineers are included. We have presented additional material at the end of chapters on matters such as calculation of the ideal-gas heat capacities and mixture vapor-liquid equilibria for polar fluids. Due to the gap between theory and practice, some compromise of rigor will be inevitable, and we are aware of the risks involved. It is hoped that future developments will make these sacrifices unnecessary.

The materials in the book were the outgrowth of lectures given for the past seven

years in a graduate course— the Modern Thermodynamics Seminar. The topics varied from year to year, reflecting the changes in interests and student needs. The main themes, however, have always revolved around the *molecular distribution functions*; i.e., treating the structure of matter in terms of the probabilistic distributions of molecules in space and time. This is the subject of statistical mechanics. The historical developments in the statistical mechanics of liquids could be summarized as (a) the partition function approach, (b) combinatorial studies, and (c) distribution function methods. Recent work has gravitated toward the last option, although the other approaches are being vigorously pursued at the same time. Partition functions are known explicitly only for very simple systems, such as the ideal gas and Ising models. For more complex systems, the approach is ineffective. Combinatorial studies were carried out, e.g., for mixture and adsorption problems (such as arrangements of polymer molecules on a lattice). The presence of sophisticated interaction forces soon taxes the combinatorial method to the limit. Distribution functions imply and implicate all these methods and more, since they are defined for any systems through a probability distribution. In principle, at least, the functions could be used for structural studies. A crucial connection is the probing of the molecular structure of matter by the scattering of x-ray and neutrons. They yield the probability distributions. These experiments lend physical support to the distribution functions. On the other hand, thermodynamic properties can be easily calculated from the probabilities. Three routes are available for this task: the energy equation, the virial equation, and the compressibility equation. These relations make the distribution functions highly useful in properties studies.

The first six chapters lead up to the integral equations. These equations are used to produce the distribution functions. Some model potentials— hard spheres and Lennard-Jones molecules— are examined. We then proceed to polar fluids and electrolyte solutions. The successful liquid state theory— the perturbation theory is introduced. For polyatomics, we offer one of the most promising approaches— the interaction site model. Interfacial behavior is investigated in a chapter on adsorption. Selected homeworks are included in the chapters. Some of these are "drill" exercises; the others are projects. To supplement the in-class experience, reading of current literature and possibly a research project applying what has been learned is recommended. In my seminar course, projects on behavior of fluids such as liquid crystals, biofluids, electrolyte solutions, and molecular sieves were assigned.

"To pursue knowledge with one's lifetime is to span the boundless by the limited... Therefore, by following the middle way, you may maintain your health, replenish your life, care for the ones you love, and live out your years." — Inner Chapter: "The Regimen of Life"

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CHAPTER I
INTRODUCTION

Democritus of Abdera: " ...οὐδὲν χρῆμα μάτην γίγνεται, ἀλλὰ πάντα ἐκ λόγου τε καὶ ὑπ᾽ ἀνάγκης"*

In this chapter, we set forth the microscopic view of matter. A material system is composed of an enormous number of particles, for example, the molecules. We call this an N-body system. The molecules interact with one another by intermolecular forces. The basic question in molecular physics is the relation between molecular interactions and the bulk properties of the system. The answer is to be found in *statistical mechanics*. Statistical mechanics is a method of accounting whereby collective microscopic states are *averaged*, resulting in macroscopically measurable quantities. As the name implies, *mechanics* deals with forces, and *statistics* is a procedure of *averaging*. Thus statistical mechanics offers a prescription for averaging the molecular forces in order to obtain values for the gross properties. The method is applicable to the study of properties of fluids, solutions, plasmas, and crystals alike, In this chapter, we shall establish the basic terminology. The mechanical variables are called dynamic variables. They are functions of the positions and motions of many bodies. The velocities and configuration constitute the *phase space*. Hamilton's equations of motion are derived that describe the time evolution of the system in phase space. The description is based on Newtonian mechanics. However, a summary of quantum mechanics is presented in Section 1.5 for comparison and later use. Other statistical concepts, such as the Gibbs ensembles and distribution functions, will be introduced in following chapters.

I.1. *The N-Body System*

An N-body system is a collection of N material particles. These particles could be molecules, charged ions, or colloidal particles. In our approach, material is considered as composed of spatially discrete units. This view is in contrast to the continuum view where matter is continuous and homogeneous. The latter view is called macroscopic. The continuum view of matter is useful in a number of engineering studies such as fluid mechanics and heat transfer. However, the microscopic view is used for the study of properties because it is necessary to understand the specific forces of interaction among the particles that compose the material. When *Newton's laws of*

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*Things do not happen fortuitously, but out of reason and necessity.

motion are applied at the molecular level, the treatment is called *classical*. When necessary, quantum mechanical corrections are incorporated. This happens at small de Broglie wavelengths (see below). For the fluids we study, a classical description is adopted whenever permissible.

The selection of the particles, whose collection constitutes the N-body system, is dictated by the particular physical process taking place. In general, we select a system of particles with maximum unity so that their internal structure and degrees of freedom have negligible effects on the physical process in progress. We illustrate this point by several simple examples.

Example 1. *Motion of a Pendulum in a Gravitational Field*

For a small ball attached to a weightless cord, the particle chosen to represent the physical system is simply the ball itself. The internal structure of the ball (whether it is made of an alloy of metals, or an aggregate of 10^{23} molecules) has no direct bearing on the motion of the pendulum.

Example 2. *The Harmonic Oscillator*

For a spring-and-block assembly, the particle is identified as the block. The spring is replaced in the physical representation by its Hookesian force.

$$F = - kx \tag{1.1}$$

i.e.

Force = $-$ (*Spring constant*)(*Displacement*)

Example 3. *Migration of Charged Particles in an Electric Field*

For the system depicted in its simplest form, the particles chosen to represent the system are the bodies carrying the electric charges. They may be dust particles, plasma, or colloidal particles in a solution.

Example 4. *Compression of Gas in a Cylinder*

The particles chosen in this case are the gas molecules inside the cylinder.

I.2. *The Hamiltonian and the Pair Potentials*

The particles in an N-body system are in constant motion undertaking movements in all directions. The total energy of the system, TE, is calculated as the sum of the kinetic contribution, KE, and the potential contribution, PE.

$$TE = KE + PE \tag{2.1}$$

The Hamiltonian, H_N, of the system is defined to be its total energy, TE, and is a function of the kinetic variables (i.e., the linear momenta $\mathbf{p}_i$) and spatial variables (e.g., the center-of-mass positions $\mathbf{r}_i$ of the particles)

$$H_N(\mathbf{p}_1, \ldots, \mathbf{p}_N, \mathbf{r}_1, \ldots, \mathbf{r}_N) = KE + PE \tag{2.2}$$

This is the Hamiltonian for an *isolated* system, i.e., there is no interaction with

surroundings, such as an isothermal bath.

KINETIC ENERGY

Kinetic energy is associated with the motion of particles. It is separated into translational, rotational, and vibrational modes.

Translational Energy

$$KE_t = \frac{1}{2} \sum_{i=1}^{N} \frac{p_i^2}{m_i} \tag{2.3}$$

Rotational Energy

$$KE_r = \frac{1}{2} \sum_{i=1}^{N} \alpha_i \cdot I_i \cdot \alpha_i \tag{2.4}$$

Vibrational Energy

$$KE_v = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{n'} m_i \omega_{ij}^2 a_{ij}^2 \tag{2.5}$$

where p_i is the momentum, m_i the mass of particle i, I_i the moment of inertia, α_i the angular velocity, ω_{ij} the frequency of vibration of mode j in molecule i, a_{ij} the amplitude of vibration, and $n' = 3n - 5$ for linear molecules and $3n - 6$ for nonlinear molecules. These classical expressions also have their quantum counterparts (see below).

POTENTIAL ENERGY

Potential energy arises due to interactions among particles and between particles and surroundings. The strength of interaction is dependent on the distances that separate these particles. The total potential energy, V_N, is a function of the spatial configuration, $r^N \equiv \{r_1, \ldots, r_N\}$, of the particles. The position of particle i, as measured from the origin, is a vector $r_i = (x_i, y_i, z_i)$. Therefore the configuration r^N is a vector of $3N$ dimensions. For nonspherical molecules, one must specify the angles of orientation for all N particles, $\{\omega_1, \ldots, \omega_N\}$, where ω_i is the set of Euler angles $(\theta_i, \phi_i, \chi_i)$ of molecule i; θ is the polar angle, ϕ the azimuthal angle, and χ the rotational angle. For structured polyatomics such as the hydrocarbon n-butane, additional coordinates are needed to uniquely determine their conformations, e.g. the cis, trans, gauche, and cyclic arrangements. In contrast to the kinetic energy, which depends on motion, the potential energy is dependent on the spatial variables of the molecules. To account for the potential energy of the N bodies, one assembles the particles into clusters of singlets, pairs, triplets, etc., and considers the total *PE* to be a sum of one-body energies, $u^{(1)}$, two-body energies, $u^{(2)}$, three-body energies, $u^{(3)}$, etc.

$$V_N(r^N, \omega^N) = \sum_{i=1}^{N} u^{(1)}(r_i, \omega_i) + \sum_{1=i<j}^{N} u^{(2)}(r_i, \omega_i, r_j, \omega_j) \tag{2.6}$$

$$+ \sum_{1=i<j<k}^{N} u^{(3)}(r_i, \omega_i, r_j, \omega_j, r_k, \omega_k) + \cdots + u^{(N)}(r^N, \omega^N)$$

We have exhibited explicitly the position and angle variables. In case there are other

spatial variables, they should also be included. The one-body potentials $u^{(1)}$ arise due to external fields (for example, an electric field). The pair potentials $u^{(2)}$ are evaluated by taking one pair of molecules at a time and measuring their interaction energy while isolated from all other molecules -- i.e., the interaction energy between a pair of particles is assumed to be undisturbed by the presence of a third particle. For example, in a system of four particles ($N=4$), we count the singlet energies $u^{(1)}(1)$, $u^{(1)}(2)$, $u^{(1)}(3)$, and $u^{(1)}(4)$, and the pair energies $u^{(2)}(12)$, $u^{(2)}(13)$, $u^{(2)}(14)$, $u^{(2)}(23)$, $u^{(2)}(24)$, and $u^{(2)}(34)$. However, in dense fluids, the sum of all these terms is not sufficient to account for the total energy of interaction. There are additional energies associated with the *residual* three-body forces. These forces are in excess of the sum of one-body and two-body forces. Thus we should also include $u^{(3)}(123)$, $u^{(3)}(124)$,..., and $u^{(3)}(234)$. Note that these higher-order forces contribute energies above and beyond the sum of pairs. The remainder is carried over to the residual four-body energies, $u^{(4)}$, excesses over the sum of energies of triplets. Finally, $u^{(N)}$ is the *excess energy* over the sum of energies of ($N-1$)-tuplets and is not the same as V_N, the *total* potential of the N-body system.

Pairwise Additivity

It is often assumed that the total *PE* is adequately given by the sum of two-body energies. This is called the *pairwise additivity* (PA) assumption

$$V_N(\mathbf{r}^N, \omega^N) \approx \sum_{i<}^{N} \sum_{j} u^{(2)}(\mathbf{r}_i, \omega_i, \mathbf{r}_j, \omega_j) \tag{2.7}$$

This assumption is valid only for dilute fluids. For argon, an accurate interaction potential valid in the liquid state is the Barker-Fisher-Watts [1] potential. It contains three-body forces. However, PA is extensively used in theoretical work to simplify treatment. Under this assumption, the Hamiltonian is

$$H_N(\mathbf{p}^N, \mathbf{r}^N, \omega^N) = \sum_{j=1}^{N} \frac{p_j^2}{2m_j} + \sum_{i<}^{N} \sum_{j} u^{(2)}(\mathbf{r}_i, \omega_i, \mathbf{r}_j, \omega_j) \tag{2.8}$$

For simplicity, we shall write $u(r)$ for $u^{(2)}(r)$. In real molecules the interaction potential is usually quite complicated. Quantum mechanical calculations exist for the most part for relatively small molecules (e.g., hydrogen [2], helium [3], and water [4]). On the other hand, simplified models are used in theoretical work. Some commonly used potentials are listed below. A detailed discussion on pair potentials is given in Appendix A.

The Ideal Gas

$$u(r) = 0 \tag{2.9}$$

The Hard Spheres (HS)

$$u(r) = +\infty, \qquad r \leq d$$
$$= 0, \qquad r > d \tag{2.10}$$

where $d=$ hard-sphere diameter.

The Square-Well Potential (SW)

$$u(r) = +\infty, \qquad r \leq d \tag{2.11}$$

$$= -\varepsilon, \qquad d < r < \lambda$$

$$= 0, \qquad r \geq \lambda$$

where $d=$ repulsive diameter, $\lambda=$ attractive diameter, and $\varepsilon=$ well depth.

The Inverse-12 Soft-Sphere Potential (SS12)

$$u(r) = 4\varepsilon(\frac{\sigma}{r})^{12} \tag{2.12}$$

where $\sigma=$ collision diameter and $\varepsilon=$ energy parameter.

The Lennard-Jones Potential (LJ)

$$u(r) = 4\varepsilon \left[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6} \right] \tag{2.13}$$

The Kihara Potential (KH)

$$u(r) = +\infty, \qquad r \leq d \tag{2.14}$$

$$= 4\varepsilon \left[\left[\frac{\sigma - d}{r - d} \right]^{12} - \left[\frac{\sigma - d}{r - d} \right]^{6} \right], \qquad r > d$$

where $d=$ the hard-core diameter.

RELATION BETWEEN THE FORCE AND THE POTENTIAL ENERGY

For a conservative system, the force acting on the system is given by the negative gradient of the potential energy

$$\mathbf{F} = -\nabla u(r) \tag{2.15}$$

This relation is general.

Example 1. The Gravitational Field

The gravitational field of the earth is conserved. We know from mechanics that the potential energy is

$$PE = u(h) = mgh = (mass)(gravity)(height) \tag{2.16}$$

Therefore the force, according to (2.15), should be

$$F = -\nabla u(h) = -\frac{\partial}{\partial h}(mgh) = -mg \tag{2.17}$$

i.e., $F = -mg$; this is precisely the expected result. The negative sign indicates that the force is acting downward (opposite to the direction of h).

Example 2. The Spring Force

A frictionless spring is a conservative system. Its potential energy is known to be

$$PE = u(x) = \frac{1}{2}kx^2 = \frac{1}{2}(spring\ constant)(displacement)^2 \tag{2.18}$$

Therefore the force on the spring is

$$F = -\frac{\partial}{\partial x}u(x) = -kx \tag{2.19}$$

This is the well-known Hookesian force.

I.3. *The Phase Space*

The dynamic state of a system of simple (structureless) particles is completely determined by specification of the positions, r_i, and momenta, p_i (i=1,...,N) of the N particles composing the system. For a three-dimensional system (with x-, y-, and z-coordinates), these $2N$ quantities (N r_i's and N p_i's) constitute a $6N$-dimensional space with coordinates

$$(r_{x1}, r_{y1}, r_{z1}, p_{x1}, p_{y1}, p_{z1},..., r_{zN}, p_{xN}, p_{yN}, p_{zN}) \tag{3.1}$$

This space is called by Gibbs [5] the *phase space* (or the Γ-space). Each point in the phase space corresponds to a particular dynamic state of the system with positions and momenta of the N particles specified by the coordinates of this chosen phase point. Since the particles are in constant motion, the movements of N particles at subsequent instants trace out, in the phase space, a continuous trajectory, which represents the history of the states of the system. All dynamic properties of the system can be inferred from its phase space trajectories. For example, the total energy, the total momentum, the collision rates, and the diffusion constant could all be obtained from the trajectories. The phase space is of great importance in statistical mechanics. We must familiarize ourselves with this concept. Let us examine some sample systems.

Example 1. One dimensional Harmonic Oscillator

For the spring-and-block system described earlier, the movement is in the x-

direction. The number of particles is $N=1$. The phase space is then two dimensional with coordinates (x, p_x). The motion of the block obeys the law of conservation of energy (assuming no frictional loss):

$$\frac{1}{2}kx^2 + \frac{1}{2}\frac{p_x^2}{m} = constant \tag{3.2}$$

The trajectory of this particle in the phase space (x, p_x) is therefore described by an ellipse.

Example 2. Pair of Charged Particles in Three-Dimensional Space

Since $N=2$, the phase space is 12 dimensional, with three components in the x-, y-, and z-directions for each of r_1, p_1, r_2, and p_2. A geometrical representation of the locus of the phase points of this system is not possible. However, the physical idea is the same as in the above example.

GENERALIZED PHASE SPACE

For polyatomic molecules the kinetic energy now comprises, in addition to the translational mode, rotational and vibrational modes. Thus KE contains

$$KE = \frac{1}{2}\sum_i^N \frac{p_i^2}{m_i} + \frac{1}{2}\sum_i^N \frac{J_i^2}{m_i} + \frac{1}{2}\sum_i^N\sum_j^{n'} m_i\omega_{ij}^2 a_{ij}^2 \tag{3.3}$$

To completely specify the dynamic state of the system, we need fix additional variables -- i.e., the angular momenta, J_i ($3N$ variables)*, the vibrational frequencies and amplitudes, $\omega_{ij}a_{ij}$ ($n'N$ variables). Now the Hamiltonian is of the form

$$TE = KE + PE = H_N(\mathbf{p}^N, \mathbf{J}^N, (\omega a)^{Nn'}, \mathbf{r}^N) \tag{3.4}$$

The dimensions of the generalized phase space are

$$3N + 3N + n'N + 3N = (n' + 9)N \tag{3.5}$$

For anisotropic molecules, the potential energy also depends on the $3N$ Euler angles of the molecules. The phase space will have $(n' + 12)N$ dimensions

$$H_N = H_N(\mathbf{p}^N, \mathbf{J}^N, (\omega a)^{Nn'}, \mathbf{r}^N, \omega^N) \tag{3.6}$$

where $\omega^N = \{\omega_1, \omega_2, ..., \omega_N\}$ and $\omega_i = (\theta_i, \phi_i, \chi_i)$ are the Euler angles of the orientation of

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*Note that the angular momentum, $\mathbf{J}_i = \{J_{ix}, J_{iy}, J_{iz}\}$, has three projections in the x-, y-, and z-directions. $\mathbf{J}_i$ is the total momentum of molecule i irrespective of its symmetry. Internally, spherical top molecules have only one value for the moment of inertia (i.e., $I_{xx} = I_{yy} = I_{zz}$), symmetrical top molecules (e.g. NH_3) have two values ($I_{xx} = I_{yy}$ and I_{zz}), and asymmetric molecules (e.g., H_2O) have three values (I_{xx}, I_{yy} and I_{zz}). They do not affect the vectorial nature (three-dimensionality) of the external total angular momentum unless the external coordinates coincide with the symmetry axes of the molecule (in which case one or two components are zero.)

molecule *i*. (We have used the symbol ω for both vibrational frequencies and Euler angles in deference to convention. The context will make the distinction clear.) In case other conformational distinctions are present, further augmentation of the dimensionality of the phase space will be required.

I.4. *The Equations of Motion*

In this section we shall derive an equation of motion which describes the time evolution of a system of *N* simple particles. Since the particles are in motion, their positions, r_i, and momenta, p_i, are functions of time:

$$\mathbf{r}_i = \mathbf{r}_i(t) \tag{4.1}$$

$$\mathbf{p}_i = \mathbf{p}_i(t), \qquad i=1,2,...,N$$

As in the mechanics for macroscopic bodies, the motion of the individual particle *i* of mass m_i is determined by Newton's second law:

$$m_i \frac{d^2\mathbf{r}_i}{dt^2} = \mathbf{F}_i \tag{4.2}$$

where $\mathbf{F}_i$ is the force acting on particle *i*. For conservative systems, the force is derived from a potential energy function. For simple systems with pair interactions only

$$\mathbf{F}_i = -\sum_{j\neq i}^{N} \nabla u(r_{ij}), \qquad r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| \tag{4.3}$$

where *u* is the interaction potential, and the gradient ∇ is with respect to $\mathbf{r}_i$. Since the momentum

$$\mathbf{p}_i = m_i \frac{d\mathbf{r}_i}{dt} \tag{4.4}$$

(4.2) can also be written as

$$\frac{d\mathbf{p}_i}{dt} = -\sum_{j\neq i}^{N} \nabla u(r_{ij}) \tag{4.5}$$

For structureless particles, H_N is a function of $\mathbf{p}_i$ and $\mathbf{r}_i$: $H_N = H_N(\mathbf{p}^N, \mathbf{r}^N)$; we can form the partial derivatives

$$\frac{\partial H_N}{\partial \mathbf{p}_i} = \frac{\mathbf{p}_i}{m_i} \tag{4.6}$$

and