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Wigner-Kirkwood expansion: Calculation of "almost classical" static properties of a Lennard-Jones many-body system

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We have applied the Wigner–distribution-function formalism for the determination of the quantum corrections, which appear in the $\hbar$ series expansion of the various "almost classical" properties of a many-body system. We have calculated the various averages which appear in the quantum corrections by means of molecular-dynamics computer simulation, up to the order $\hbar^6$ for the case of Boltzmann particles interacting via a Lennard-Jones potential. Here we report the results of the calculation for the potential and kinetic energies, for the pressure, for the free energy, and for the radial distribution function $g(r)$ at nine different thermodynamic points. The application to the case of He, Ne, Ar, H_2, and D_2 are given whenever the $\hbar$ series expansion can be considered convergent. The advantages and disadvantages of our method are also discussed.

I. INTRODUCTION

The development of fast computer facilities together with the use of the Monte Carlo and molecular-dynamics methods have permitted in the last ten years the calculation of an enormous amount of properties, in almost all the thermodynamic points of the gas, liquid, and solid states of N-body systems within the framework of "classical mechanics." In particular, once a model is given for the interaction potential of the N-body system, the results of the computer simulation can be considered practically rigorous, within the limitation of the model potential itself, for those properties for which the thermodynamic limit is met by the number of molecules used in the computation. A similar program cannot be carried out as far in the framework of quantum mechanics, given the present computer facilities. In fact, neither the determination of the matrix elements of the statistical operator $\underline{\rho}$ in the canonical ensemble nor the solution of the Schrödinger equation for an N-body system at finite thermodynamic conditions has been achieved on a rigorous numerical level. However, recently, three different methods have been used in order to perform approximate calculations for quantum-mechanical properties of an N-body system:

(1) The Wigner-Kirkwood approach of expanding a quantum property in terms of $\hbar$, where $\hbar = h/2\pi$ and h is Planck's constant, combined with classical molecular dynamics, has been applied to the determination of quantum corrections to "almost classical" properties;[1-5]

(2) The application of the path-integral method together with a sophisticated form of the Metropolis Monte Carlo technique has been used to determinate averages over the diagonal matrix elements of $\underline{\rho}$ of quantum systems at finite temperature;[6,7]

(3) The solution of an approximate Schrödinger equation for N interacting Gaussian wave packets has been attempted in order to also derive dynamical properties.[8]

The third method, due to the great difficulty of choosing the wave packets which are used instead of point particles for studying dynamical behavior in an optimal way, is still at a preliminary level and cannot be applied in a routine way to the determination of properties of "real" systems.

The second method is in principle the solution of the problem. However, it requires approximations which are not fully tested, as pointed out in Ref. 7(b); moreover, at present it requires some skill in the use of the modified Metropolis Monte Carlo method[6] for the production of the various integration paths in the $3N$-dimensional configuration space. It also requires an approximate form of the high-temperature N-body off-diagonal matrix elements of $\underline{\rho}$, the justification of which mostly relies on the goodness of the final results. With this method Ceperley and Pollock have been able to calculate the properties of ^{4}He even in the neighborhood of the λ transition.[6]

The first method is the one we have recently been using extensively for the determination of quantum corrections to the classical behavior for various "almost classical" properties of N-body systems. The disadvantage of this method consists in the fact that it is limited to systems and thermodynamic situations for which the $\hbar$ expansion of the property under study is found to converge, which is the meaning we attribute to the words "almost classical."

The advantages are at present two: The first is that, when the $\hbar$ series expansion is convergent, no approximations are necessary to carry out the calculation; secondly, since the calculation of quantum corrections is performed within the classical framework, a number of properties can be calculated simultaneously with the same set of statistical points in the $6N$-dimensional phase space of the system. Moreover, since the reduced value of $\hbar$ does not enter explicitly in the computation, the results can be interpreted as pertaining to different substances as long as they are described by the same type of potential (e.g., Lennard-Jones). The computation time is comparable to the one used in method (2) which yields only a few properties depending on positions only.

In previous papers we have calculated quantum corrections for the moments of interaction-induced spectra[3] and for the pair distribution function of a system of particles interacting with a pairwise additive Lennard-Jones potential.[4,5] Here we report the results of a comprehensive calculation of quantum corrections for the internal energy, kinetic energy, pressure, and radial distribution function of the Lennard-Jones system at nine different thermodynamic points. The quantum corrections to the pair distribution function have been calculated up to the term of order $\hbar^6$ at six thermodynamic points, the other properties only up to $\hbar^4$ term.

We have chosen to use the Lennard-Jones pair potential again, because it is a realistic potential for a large number of systems, which, even though not very refined, give qualitative, and often satisfactorily quantitative, agreement between calculated and experimental values. Moreover, this potential is simple enough to reduce the very long computational time of the quantum corrections, and it has been widely used in classical calculations of any kind of properties which renders it a reference potential.

In order to derive the explicit functional expressions for the various quantum corrections which are then used in the computations, two methods have been used. Section II of this paper describes the first method in its generality, which is based on Wigner's original idea of 1932,[9] and gives the expression of the first three quantum corrections to the Wigner distribution function in the full classical phase space. Section IV gives the results of the second method, which is based on a linked-graph resummation procedure, developed by Fujiwara, Osborne, and Wilk,[10] for the determination of the quantum corrections to the Wigner distribution function in the configuration subspace. In this paper we refer only to particles following Boltzmann's statistics, even though the method in principle could be applied to particles following quantum statistics. The main purpose of our effort here is to show the possibilities and the limitation of the Wigner-Kirkwood expansion for the calculation of a wide range of static properties of an N-body system.

II THE WIGNER DISTRIBUTION FUNCTION: DEFINITION AND PROPERTIES

In this section, for the sake of completeness and in order to establish notations, we recall a few general expressions[11,12] concerning the Wigner-Kirkwood approach.[9] The quasiprobability distribution function introduced by Wigner[9] permits us to establish a correspondence between operators in quantum mechanics and c functions which are defined in the classical phase space. This correspondence means in practice that if $\underline{A}(\underline{R},\underline{P})$ is an operator corresponding to an observable of an N-body quantum system ($\underline{R}$ and $\underline{P}$ are position and momentum operators in $3N$ dimensions), its average value can be written as

$$\langle \underline{A} \rangle = \mathrm{Tr}(\underline{\rho}\,\underline{A}) = (1/h)^{3N} \int d\hat{r} \int d\hat{p}\, \rho_W(\hat{r},\hat{p}) A_W(\hat{r},\hat{p}) \ , \tag{2.1}$$

where $\hat{r}$ and $\hat{p}$ are the $3N$-dimensional variables (c-numbers) of the classical phase space which correspond to the quantum operators $\underline{R}$ and $\underline{P}$, and ρ is the density matrix operator which, for a system in thermodynamic equilibrium, is defined as

$$\underline{\rho} = e^{-\beta \underline{H}} / Z \ , \tag{2.2}$$

with

$$Z = \mathrm{Tr}(e^{-\beta \underline{H}}) \ , \tag{2.3}$$

while $\underline{H}$ is the Hamiltonian operator of the system.

In the expression (2.1) $\rho_W(\hat{r},\hat{p})$ is the Wigner distribution function while $A_W(\hat{r},\hat{p})$ is the function which corresponds to the operator $\underline{A}$ and, as proposed by Weyl[13] and demonstrated by Moyal,[14] is defined as

$$A_W(\hat{r},\hat{p}) = \int d\hat{z} \exp(i\hat{p}\,\hat{z}/\hbar) \times \langle \hat{r} - \hat{z}/2 \,|\, \underline{A}(\underline{R},\underline{P}) \,|\, \hat{r} + \hat{z}/2 \rangle \ . \tag{2.4}$$

Here $\hat{p}\,\hat{z}$ indicates the scalar product between two $3N$-dimensional vectors.

Two important properties of the Wigner distribution ρ_W and of the Weyl-Wigner equivalent (W-equivalent) A_W, respectively, which will be useful in the following, are

(1) The integration with respect to the variables $\hat{p}$ of $h^{-3N} A_W(\hat{r},\hat{p})$ gives the diagonal matrix elements of $\underline{A}$, i.e.,

$$A_W(\hat{r}) = (1/h)^{3N} \int d\hat{p}\; A_W(\hat{r},\hat{p}) = \langle \hat{r} \,|\, \underline{A} \,|\, \hat{r} \rangle \ . \tag{2.5}$$

(2) The W-equivalent of an operator $\underline{A}$ which depends only on either $\underline{R}$ or $\underline{P}$ is simply the classical variable $A(\hat{r})$ or $A(\hat{p})$ itself, i.e.,

$$\text{If } \underline{A} = \underline{A}(\underline{R}), \text{ then } A_W(\hat{r}) = A(\hat{r}) \ ; \tag{2.6a}$$

$$\text{if } \underline{A} = \underline{A}(\underline{P}), \text{ then } A_W(\hat{p}) = A(\hat{p}) \ . \tag{2.6b}$$

Both properties (1) and (2) can be derived immediately from Eq. (2.4). These two properties greatly simplify the calculation of the average value of the operator $\underline{A}(\underline{R})$ and $\underline{A}(\underline{P})$ with the Wigner method. In fact, for such operators, we have from Eqs. (2.1), (2.5), and (2.6)

$$\langle \underline{A}(\underline{R}) \rangle = \int d\hat{r}\, \rho_W(\hat{r}) A(\hat{r}) \ , \tag{2.7a}$$

$$\langle \underline{A}(\underline{P}) \rangle = (1/h)^{3N} \int d\hat{r} \int d\hat{p}\, \rho_W(\hat{r},\hat{p}) A(\hat{p}) \ . \tag{2.7b}$$

Therefore, the only quantities we have to determine in order to perform the averages (2.7) are $\rho_W(\hat{r},\hat{p})$ and $\rho_W(\hat{r})$.

There exists one method to determine an explicit expression for $\rho_W(\hat{r},\hat{p})$ and two methods for $\rho_W(\hat{r})$, once a model Hamiltonian is given for the system under consideration. The first one is based on the solution of the Bloch equation for $\rho_W(\hat{r},\hat{p})$,[11] successive integration of which over the $\hat{p}$ variable then gives $\rho_W(\hat{r})$. The second, developed by Fujiwara, Osborne, and Wilk,[10] gives only the possibility of calculating the various contribution to the diagonal and off-diagonal matrix elements of ρ by means of a linked-graph resummation procedure. Both methods ultimately lead to a representation of $\rho_W(\hat{r})$ as a series expansion with respect to $\hbar$. In the following two sections we will give a few details about the two methods since we have used both of them in order to derive the explicit expression of the coefficient of $\hbar^6$ in the $\hbar$ expansion of $\rho_W(\hat{r})$.

III. QUANTUM CORRECTIONS TO THE WIGNER DISTRIBUTION FUNCTION

Let us start from the definition (2.4) of the Weil-Wigner equivalent. If we take into account the property that the W-equivalent of a product of two operators, $\underline{A}\ \underline{B}$, is[11]

$$(\underline{A}\ \underline{B})_W = A_W \exp(\hbar\Lambda/2i) B_W \ , \tag{3.1}$$

where Λ is the classical Poisson-bracket operator

$$\Lambda = \overleftarrow{\nabla}_{\hat{p}} \overrightarrow{\nabla}_{\hat{r}} - \overleftarrow{\nabla}_{\hat{r}} \overrightarrow{\nabla}_{\hat{p}} \ , \tag{3.2}$$

then from the Bloch equation for the operator $\underline{\Omega} = \exp(-\beta\underline{H})$ we can write an equation for Ω_W, i.e.,[11]

$$\frac{\partial}{\partial\beta}\Omega_W(\hat{r},\hat{p}) = -H_W \cos(\hbar\Lambda/2)\Omega_W(\hat{r},\hat{p}) \ , \tag{3.3}$$

where H_W is the Weyl-Wigner equivalent of the Hamiltonian $\underline{H}$ and the classical operator $\cos(\cdots)$ is defined by means of its series expansion. The solution of Eq. (3.3), which can be obtained by series expanding $\Omega_W(\hat{r},\hat{p})$ with respect to $\hbar$, gives the possibility of explicitly writing the function coefficients of the various powers of $\hbar$ in the expansion of $\Omega_W(\hat{r},\hat{p})$.

Here we will consider an N-body system of identical particles with an Hamiltonian of the form

$$\underline{H}(\underline{R},\underline{P}) = \frac{\underline{P}^2}{2m} + \Phi(\underline{R}) \ . \tag{3.4}$$

Therefore, from the property (2.6) its W-equivalent is

$$H_W(\hat{r},\hat{p}) = H(\hat{r},\hat{p}) = \frac{\hat{p}^2}{2m} + \Phi(\hat{r}) \ , \tag{3.5}$$

where m is the mass of the particles and $\Phi(r)$ is the total interaction potential. In this case $\Omega_W(\hat{r},\hat{p})$ can be written as

$$\Omega_W(\hat{r},\hat{p}) = e^{-\beta H(\hat{r},\hat{p})}\chi(\hat{r},\hat{p}) \ , \tag{3.6}$$

where

$$\chi(\hat{r},\hat{p}) = 1 + \hbar^2\chi_1(\hat{r},\hat{p}) + \hbar^4\chi_2(\hat{r},\hat{p}) + \hbar^6\chi_3(\hat{r},\hat{p}) + O(\hbar^8) \ , \tag{3.7}$$

while from Eq. (2.3) the partition function is

$$Z = \mathrm{Tr}(\underline{\Omega}) = (1/h)^{3N}\int d\hat{r}\, d\hat{p}\, \Omega_W(\hat{r},\hat{p}) \ . \tag{3.8}$$

We have derived the expressions for $\chi_1(\hat{r},\hat{p})$, $\chi_2(\hat{r},\hat{p})$, and $\chi_3(\hat{r},\hat{p})$ by means of the procedure indicated above. For the sake of completeness we give here these expressions in terms of the $3N$ components p_i of $\hat{p}$ and of the components of the gradients of various order of Φ, defining the component of a gradient of nth order $(\nabla_1\nabla_2\cdots\nabla_n)\phi$ as

$$\Phi_{i_1 i_2 \cdots i_n} = \frac{\partial^n}{\partial r_{i_1}\partial r_{i_2}\cdots\partial r_{i_n}}\Phi(\hat{r}) \ , \tag{3.9}$$

where r_{i_h} is the i_hth component of $\hat{r}$ ($i_h = 1,2,\ldots,3N$). With those notations $\chi_1(\hat{r},\hat{p})$ is given by

$$\chi_1(\hat{r},\hat{p}) = \frac{1}{24m}\left[\frac{\beta^3}{m}p_i p_j \Phi_{ij} - 3\beta^2\Phi_{ii} + \beta^3\Phi_i\Phi_i\right] \ , \tag{3.10}$$

where summations with respect to the repeated indexes must be performed over the $3N$ components of $\hat{p}$ and $\hat{r}$. The rather complicated expressions of $\chi_2(\hat{r},\hat{p})$ and $\chi_3(\hat{r},\hat{p})$ are given in the Appendix. Both $\chi_1(\hat{r},\hat{p})$ and $\chi_2(\hat{r},\hat{p})$ are taken from Ref. 2 while $\chi_3(\hat{r},\hat{p})$ is new. From the definitions (2.2) and (2.3) and by means of $\Omega_W(\hat{r},\hat{p})$ we can now write $\rho_W(\hat{r},\hat{p})$ as a ratio between two series expansion in terms of $\hbar$, i.e.,

$$\rho_W(\hat{r},\hat{p}) = \frac{\Omega_W(\hat{r},\hat{p})}{(1/h)^{3N}\int d\hat{p}\int d\hat{r}\,\Omega_W(\hat{r},\hat{p})} \ , \tag{3.11}$$

or, using Eq. (3.6),

$$\rho_W(\hat{r},\hat{p}) = \frac{e^{-\beta H(\hat{r},\hat{p})}\chi(\hat{r},\hat{p})}{N!Z_\Gamma\langle\chi(\hat{r},\hat{p})\rangle_\Gamma} \ , \tag{3.12}$$

where Z_Γ is the classical partition function

$$Z_\Gamma = (N!h^{3N})^{-1}\int d\hat{r}\int d\hat{p}\, e^{-\beta H(\hat{r},\hat{p})} \tag{3.13}$$

and $\langle\cdots\rangle_\Gamma$ indicates an average performed with respect to the distribution function in the classical phase space (subscript Γ). Applying Eq. (2.5) to (3.12), and using the relation between the classical partition function Z_Γ and the configuration integral Q_c which is defined as

$$Q_c = (1/N!)\int d\hat{r}\, e^{-\beta\Phi(\hat{r})} \ , \tag{3.14}$$

we then have

$$\rho_W(\hat{r}) = \left[\frac{2\pi\hbar^2}{mk_BT}\right]^{3N/2}\frac{\Omega_W(\hat{r})}{N!Q_c\langle\chi(\hat{r})\rangle_c} \ . \tag{3.15}$$

In the last equation $\langle\cdots\rangle_c$ is the average in the classical configuration space (subscript c), while, in agreement with Eq. (2.5),

$$\Omega_W(\hat{r}) = h^{-3N}\int d\hat{p}\,\Omega_W(\hat{r},\hat{p}) = \langle\hat{r}\,|\,\underline{\Omega}\,|\,\hat{r}\rangle \tag{3.16}$$

is the diagonal matrix element of Ω and

$$\chi(\hat{r}) = 1 + \hbar^2\chi_1(\hat{r}) + \hbar^4\chi_2(\hat{r}) + \hbar^6\chi_3(\hat{r}) + O(\hbar^8) \ , \tag{3.17}$$

with $\chi_n(\hat{r})$ defined as

$$\chi_n(\hat{r})=(2\pi m k_B T)^{-3N/2}\int d\hat{p}\, e^{-\beta(\hat{p}^2/2m)}\chi_n(\hat{r},\hat{p}) \ , \qquad (3.18)$$

which also ensures that $\langle \chi_n(\hat{r})\rangle_c=\langle \chi_n(\hat{r},\hat{p})\rangle_\Gamma$. By means of Eqs. (3.6), (3.7), and (3.16)–(3.18), we also can write

$$\Omega_W(\hat{r})=\left[\frac{mk_BT}{2\pi\hbar^2}\right]^{3N/2} e^{-\beta\Phi(\hat{r})}\chi(\hat{r}) \ . \qquad (3.19)$$

Therefore, from Eqs. (3.15) and (3.19) the diagonal matrix elements of $\underline{\rho}$ becomes

$$\rho_W(\hat{r})=\frac{e^{-\beta\Phi(\hat{r})}\chi(\hat{r})}{N!Q_c\langle\chi(\hat{r})\rangle_c} \ . \qquad (3.20)$$

Finally, using (3.8), (3.16), (3.19), and (3.14) and dividing by $N!$, we have that the partition function Z, for particles following the Boltzmann statistics, can be written as

$$Z=\left[\frac{mk_BT}{2\pi\hbar^2}\right]^{3N/2}\langle\chi(\hat{r})\rangle_c Q_c \ . \qquad (3.21)$$

IV. FUJIWARA, OSBORNE, AND WILK RESUMMATION OF THE WIGNER EXPANSION OF $\langle r \mid \underline{\Omega} \mid r \rangle$ (REF. 10)

An alternative way of deriving the various terms in the $\hbar$ expansion of $\rho_W(\hat{r})$ is to apply the result of the linked-graph method developed in Ref. 10, which permits us to write the diagonal matrix elements of $\underline{\Omega}$ as an exponentiated series expansion with respect to $\hbar$. From the paper of Fujiwara *et al.* we have, using the expansion parameter $q=\hbar^2/2m$,

$$\begin{aligned}\langle\hat{r}\mid\underline{\Omega}\mid\hat{r}\rangle&=\left[\frac{mk_BT}{2\pi\hbar^2}\right]^{3N/2} e^{-\beta\Phi(\hat{r})}e^{[qS_1(\hat{r})+q^2S_2(\hat{r})+q^3S_3(\hat{r})+O(q^4)]}\\&=\left[\frac{mk_BT}{2\pi\hbar^2}\right]^{3N/2} e^{-\beta\Phi(\hat{r})}\{1+qS_1(\hat{r})+q^2[S_2(\hat{r})+\tfrac{1}{2}S_1^2(\hat{r})]+q^3[S_3(\hat{r})+S_1(\hat{r})S_2(\hat{r})+\tfrac{1}{6}S_1^3(\hat{r})]+O(q^4)\} \ .\end{aligned}$$

Therefore, comparing Eq. (3.19) with (4.1), we find

$$\chi_1(\hat{r})=\frac{1}{2m}S_1(\hat{r}) \ , \qquad (4.2)$$

$$\chi_2(\hat{r})=\frac{1}{4m^2}[S_2(\hat{r})+\tfrac{1}{2}S_1^2(\hat{r})] \ , \qquad (4.3)$$

$$\chi_3(\hat{r})=\frac{1}{8m^3}[S_3(\hat{r})+S_1(\hat{r})S_2(\hat{r})+\tfrac{1}{6}S_1^3(\hat{r})] \ . \qquad (4.4)$$

Here the functions $S_n(\hat{r})$ are given as linear-path integrals of the form

$$S_1(\hat{r})=-\beta^2\int_0^1 d\xi_1\, c_1\Phi(\hat{r}_1)+\beta^3\int_0^1 d\xi_1\int_0^1 d\xi_2\, b_{12}\Phi(\hat{r}_1)\Phi(\hat{r}_2) \ , \qquad (4.5)$$

$$\begin{aligned}S_2(\hat{r})=&-\tfrac{1}{2}\beta^3\int_0^1 d\xi_1\, c_1^2\Phi(\hat{r}_1)+\beta^4\int_0^1 d\xi_1\int_0^1 d\xi_2(b_{12}c_2+b_{12}^2)\Phi(\hat{r}_1)\Phi(\hat{r}_2)\\&-\tfrac{2}{3}\beta^5\int_0^1 d\xi_1\int_0^1 d\xi_2\int_0^1 d\xi_3(b_{12}b_{13}+b_{12}b_{23}+b_{13}b_{23})\Phi(\hat{r}_1)\Phi(\hat{r}_2)\Phi(\hat{r}_3) \ , \qquad (4.6)\end{aligned}$$

and[15]

$$\begin{aligned}S_3(\hat{r})=&-\frac{\beta^4}{3!}\int_0^1 d\xi_1\, c_1^3\Phi(\hat{r}_1)+\frac{\beta^5}{2!}\int_0^1 d\xi_1\int_0^1 d\xi_2\left[\frac{2^3}{3!}b_{12}^3+\frac{2^2}{2!}b_{12}^2c_2+\frac{2}{2!}b_{12}c_2^2\right]\Phi(\hat{r}_1)\Phi(\hat{r}_2)\\&-\frac{\beta^6}{3!}\int_0^1 d\xi_1\int_0^1 d\xi_2\int_0^1 d\xi_3[4(b_{12}^2b_{13}+b_{12}^2b_{23}+b_{13}^2b_{23})+4(b_{12}b_{13}^2+b_{12}b_{23}^2+b_{13}b_{23}^2)\\&\qquad+4(b_{12}b_{13}+b_{12}b_{23}+b_{13}b_{23})c_2+2^3(b_{12}b_{13}b_{23})]\,\Phi(\hat{r}_1)\Phi(\hat{r}_2)\Phi(\hat{r}_3)\\&+\frac{\beta^7}{4!}\int_0^1 d\xi_1\int_0^1 d\xi_2\int_0^1 d\xi_3\int_0^1 d\xi_4\, 2^3\sum_{\left\{\sum_{i,j}l_{ij}=3;0\le l_{ij}\le 1\right\}}(b_{12}^{l_{12}}b_{23}^{l_{23}}b_{34}^{l_{34}}b_{14}^{l_{14}}b_{13}^{l_{13}}b_{24}^{l_{24}})\,\Phi(\hat{r}_1)\Phi(\hat{r}_2)\Phi(\hat{r}_3)\Phi(\hat{r}_4) \ . \qquad (4.7)\end{aligned}$$

The summation in the last term of Eq. (4.7) must be performed over all possible combinations of the integer powers l_{ij}, with the restrictions that the sum of all l_{ij} is 3 while l_{ij} itself can be either 0 or 1.

Moreover, in Eqs. (4.5)–(4.7) the quantities c_i and b_{ij} are classical operators defined as

$$\begin{aligned}c_i&=\sum_{j=1}^{i}(1-\xi_j)\xi_j\nabla_j^2 \ ,\\b_{ij}&=\xi_<(1-\xi_>)\nabla_i\cdot\nabla_j \ ,\end{aligned}\qquad (4.8)$$

where the symbols $<$ and $>$ stand for the smaller and greater, respectively, of the indexes i and j. Note that i

and j are not particle indices, but identifiers denoting on which variable each differential operator is supposed to act. Thus ∇_n is a full $3N$-dimensional gradient operator acting only on $\hat{r}_n$, and after this operation $\hat{r}_n$ is set equal to $\hat{r}$ in Eqs. (4.5)–(4.7). By means of these equations we have derived the explicit expressions for S_1, S_2, and S_3. For the sake of completeness we report here all three expressions, the first two of which have already been given in Ref. 11 while the third is new. We have then

$$S_1(\hat{r})=\tfrac{1}{12}\beta^3\Phi_i\Phi_i-\tfrac{1}{6}\beta^2\Phi_{ii}\ , \tag{4.9}$$

$$S_2(\hat{r})=-\tfrac{1}{60}\beta^5\Phi_{ik}\Phi_i\Phi_k+\beta^4(\tfrac{1}{30}\Phi_{ikk}\Phi_i+\tfrac{1}{90}\Phi_{ik}\Phi_{ik})$$
$$-\tfrac{1}{60}\beta^3\Phi_{ikik}\ , \tag{4.10}$$

with the convention of summation over repeated indexes (now denoting the $3N$ components of $\hat{r}$). The more complicated expression for $S_3(\hat{r})$ is given in the Appendix.

By means of (4.2)–(4.4) and of (4.9), (4.10), and (A30)–(A34) we can now easily derive $\chi_1(\hat{r})$, $\chi_2(\hat{r})$, and $\chi_3(\hat{r})$. We have verified that these expressions are identical to those that can be derived from Eqs. (3.10) and (A1)–(A12) by averaging over the p variables [see Eq. (3.18)]. This check is of particular importance for $\chi_3(\hat{r})$ which is quite complex.

V. QUANTUM CORRECTIONS TO MANY-BODY PROPERTIES

From the results of Secs. III and IV we readily obtain expressions for the quantum corrections to the various properties of the system which we are interested in. In particular for operators $A(\underline{R})$ depending only on $\underline{R}$ we have, by means of Eqs. (2.7a) and (3.20)

$$\langle \underline{A}(\underline{R})\rangle=\frac{\langle A(\hat{r})\chi(\hat{r})\rangle_c}{\langle \chi(\hat{r})\rangle_c}\ . \tag{5.1}$$

Using Eq. (3.17), the series expansion of (5.1), up to order $\hbar^6$, can be written as

$$\langle \underline{A}(\underline{R})\rangle=\langle A(\hat{r})\rangle_c+\hbar^2\langle A(\hat{r})\rangle_1+\hbar^4\langle A(\hat{r})\rangle_2$$
$$+\hbar^6\langle A(\hat{r})\rangle_3+\cdots\ , \tag{5.2}$$

where

$$\langle A(\hat{r})\rangle_1=\langle A(\hat{r})\chi_1(\hat{r})\rangle_c-\langle A(\hat{r})\rangle_c\langle \chi_1(\hat{r})\rangle_c\ , \tag{5.3}$$

$$\langle A(\hat{r})\rangle_2=\langle A(\hat{r})\chi_2(\hat{r})\rangle_c-\langle A(\hat{r})\rangle_c\langle \chi(\hat{r})\rangle_c$$
$$-\langle A(\hat{r})\rangle_1\langle \chi_1(\hat{r})\rangle_c\ , \tag{5.4}$$

$$\langle A(\hat{r})\rangle_3=\langle A(\hat{r})\chi_3(\hat{r})\rangle_c-\langle A(\hat{r})\rangle_c\langle \chi_3(\hat{r})\rangle_c$$
$$-\langle A(\hat{r})\rangle_1\langle \chi_2(\hat{r})\rangle_c-\langle A(\hat{r})\rangle_2\langle \chi_1(\hat{r})\rangle_c\ . \tag{5.5}$$

Similarly, for operators which depend only on $\underline{P}$ variable, i.e., $\underline{A}=\underline{A}(\underline{P})$, from Eqs. (2.7b) and (3.12) we have

$$\langle \underline{A}(\underline{P})\rangle=\frac{\langle A(\hat{p})\chi(\hat{r},\hat{p})\rangle_\Gamma}{\langle \chi(\hat{r},\hat{p})\rangle_\Gamma}\ . \tag{5.6}$$

Using now Eq. (3.7) the series expansion of Eq. (5.6), up to order $\hbar^6$, can be written as

$$\langle \underline{A}(\underline{P})\rangle=\langle A(\hat{p})\rangle_\Gamma+\hbar^2\langle A(\hat{p})\rangle_1+\hbar^4\langle A(\hat{p})\rangle_2$$
$$+\hbar^6\langle A(\hat{p})\rangle_3+\cdots\ , \tag{5.7}$$

where

$$\langle A(\hat{p})\rangle_1=\langle A(\hat{p})\chi_1(\hat{r}_1\hat{p})\rangle_\Gamma-\langle A(\hat{p})\rangle_\Gamma\langle \chi_1(\hat{r},\hat{p})\rangle_\Gamma\ , \tag{5.8}$$

$$\langle A(\hat{p})\rangle_2=\langle A(\hat{p})\chi_2(\hat{r},\hat{p})\rangle_\Gamma-\langle A(\hat{p})\rangle_\Gamma\langle \chi_2(\hat{r},\hat{p})\rangle_\Gamma$$
$$-\langle A(\hat{p})\rangle_1\langle \chi_1(\hat{r},\hat{p})\rangle_\Gamma\ , \tag{5.9}$$

$$\langle A(\hat{p})\rangle_3=\langle A(\hat{p})\chi_3(\hat{r},\hat{p})\rangle_\Gamma-\langle A(\hat{p})\rangle_\Gamma\langle \chi_3(\hat{r},\hat{p})\rangle_\Gamma$$
$$-\langle A(\hat{p})\rangle_1\langle \chi_2(\hat{r},\hat{p})\rangle_\Gamma$$
$$-\langle A(\hat{p})\rangle_2\langle \chi_1(\hat{r},\hat{p})\rangle_\Gamma\ . \tag{5.10}$$

We recall that the subscript Γ implies an average over all $6N$ dimensions of the classical phase space.

On the basis of Eqs. (5.2)–(5.10) we have calculated, for the Lennard-Jones system, quantum corrections for various thermodynamic properties such as the total and kinetic energies, the free energy, and the pressure, and also for the pair distribution function $g(r)$, at various thermodynamic points, performing the classical averages by means of molecular-dynamics simulations. The expressions of $\langle \chi_n(\hat{r},\hat{p})\rangle_\Gamma=\langle \chi_n(\hat{r})\rangle_c$ which we have used in the calculation are also reported in the Appendix. The results of these calculations are given in the following sections.

VI. MOLECULAR-DYNAMICS SIMULATIONS AND THERMODYNAMIC STATES

As mentioned before, all classical averages which are needed for the calculation of quantum corrections have been obtained by means of molecular-dynamics computer simulations, at various thermodynamic points, of an N-body system described by a pairwise additive Lennard-Jones potential. The computer simulations have been performed with the Verlet algorithm with a reduced time step Δt^* ranging from 0.005 to 0.001 depending on temperature. Runs of several 100 000 time steps had to be made to ensure satisfactory convergence of the results. Usually we have worked with 108 particles and cubic boundary conditions with a force cutoff r_c equal to half the box length. Since the calculation of the $\hbar^6$ correction to $g(r)$, i.e., $g_3(x)$, is very time consuming, a rhombic dodecahedron was chosen as the basic cell in most of these simulations because it allows one to work with a smaller number of particles while still maintaining a minimum interaction cutoff of 2.5 particle diameters. This leads to considerable saving in computer time since the calculation of the correction term $g_3(x)$, involving three-body sums, is proportional to N^3.

Table I gives the details of the calculations at various thermodynamic points. In order to gain information about temperature and density dependence, some of the runs were made either at the same density or at the same temperature. The point $T^*=5$, $\rho^*=0.365$ has been chosen in order to compare our results with Pollock and Ceperley's[6] PIMC (path-integral Monte Carlo) simula-

TABLE I. Details of various molecular-dynamics runs. T^* and ρ^* are reduced temperature and density, respectively. N is the number of atoms in the simulation. The boundary conditions (BC) were either cubic (C) or rhombic dodecahedral (RHD). T_c^* is the critical temperature, which for a classical L-J system is 1.35.

Run	T^*	ρ^*	N	Time	BC	Comments
1a	0.52	1.005	108	2.5×10^{5}	C	solid
1b			256	8.0×10^{4}	C	
2	1.35	0.964	108	7.0×10^{5}	C	liquid in coexistence with solid
3a	0.75	0.833	108	1.25×10^{6}	C	liquid at triple point
3b			74	2.5×10^{5}	RD	
4a	0.98	0.694	64	2.9×10^{5}	RD	liquid in coexistence with gas
4b			108	5.0×10^{5}	C	
5	1.35	0.694	108	5.0×10^{5}	C	liquid
6a	1.15	0.61	108	2.0×10^{5}	C	liquid in coexistence with gas
6b			64	1.1×10^{5}	RD	
7a	1.7	0.35	256	2.0×10^{5}	C	critical density, $T^*=1.3T_c^*$
7b			108	2.5×10^{5}	C	
7c			32	1.4×10^{5}	RD	
8a	3.0	0.35	108	6.0×10^{5}	C	critical density, $T^*=2.3T_c^*$
8b			44	2.5×10^{5}	RD	
9a	5.0	0.365	64	1.0×10^{5}	RD	as thermodynamic point as
9b			32	2.5×10^{5}	RD	Pollock and Ceperley for helium (Ref. 6)

tions for helium. The results pertaining to the pair correlation function at $T^*=0.98$ and $\rho^*=0.694$ have been partly used in a recent comparison of the Wigner-Kirkwood corrected $g(r)$ with the experimental results for neon.[5] In order to generate sufficient statistics, the typical length of the runs had to be of the order of several hundred thousand time steps. Moreover, since the corrections to the pair distribution function turned out to be quite affected by statistical noise, we have often performed runs with different numbers of particles to average out spurious structures at long range.

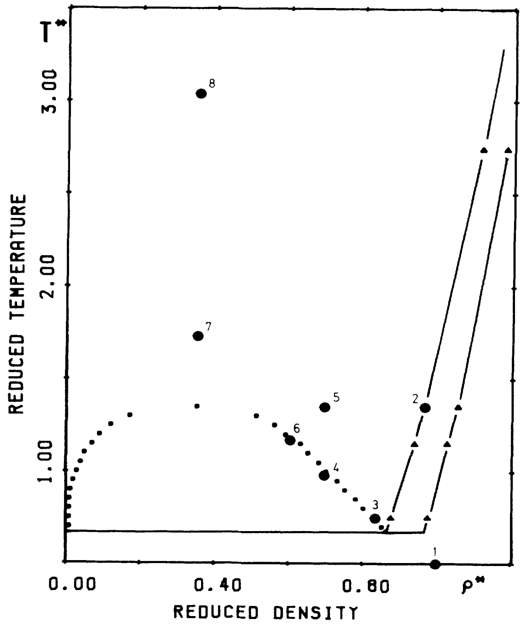

FIG. 1. Phase diagram for a classical Lennard-Jones system. Small dots indicate the liquid-gas coexistence line and were obtained from the equation of state given in Ref. 16. The melting lines are drawn through the data of Ref. 17 (triangles). The horizontal line marks the triple point temperature. The large dots illustrate the positions of our simulations in the phase diagram.

The thermodynamic points were chosen such as to cover a wide range of thermodynamic states. Figure 1 shows the phase diagram for a classical Lennard-Jones system calculated from the equation of state of Nicholas *et al.*[16] and the column of comments in Table I refers to this classical diagram.

The simulations were performed on various computers located either in Wien (VAX 11/750 at the Prozessrechenanlage Physik) or Firenze (VAX 11/750 at the Astronomy Department, GOULD/S.E.L. MPX-32 at the Physics Department). One run (No. 6b) was performed on CINECA's CRAY/XMP at Bologna in order to establish some comparison in execution speed.

VII. RESULTS FOR THE QUANTUM CORRECTIONS OF THERMODYNAMIC PROPERTIES

We have used expressions (5.2)–(5.5) and (5.7)–(5.10) for the calculation of the quantum corrections to the total energy U, kinetic energy K, pressure p, and Eq. (3.21) for the free energy F of an N-body system at various thermodynamic conditions up to order $\hbar^4$. This has been done by calculating, in the molecular-dynamics simulations, the classical averages which appear in these expressions together with, and much in the same way as, the classical values of U, K, and p. The N-body interaction potential used in the computer simulations is the pairwise additive (6-12) Lennard-Jones potential:

$$\Phi(\hat{r})=\sum_{i=1}^{N}\sum_{j=i+1}^{N}\phi(r_{ij}) , \tag{7.1}$$

where r_{ij} is the distance between particles i and j, and

$$\phi(r_{ij})=4\epsilon[(\sigma/r_{ij})^{12}-(\sigma/r_{ij})^{6}] \ . \tag{7.2}$$

This has been used in the reduced form

$$\Phi^*=\sum_{i=1}^{N}\sum_{j=i+1}^{N}\phi^*(x_{ij}) \ , \tag{7.3}$$

where

$$\phi^*(x_{ij})=\frac{1}{\epsilon}\phi(r_{ij}/\sigma) \ .$$

All quantities have been calculated in reduced units and the extensive quantities are given per particle; therefore, the calculation gives $E^*/N=E/N\epsilon$, $K^*/N=K/N\epsilon$, $p^*=p\sigma^3/\epsilon$, and $F^*/N=F/N\epsilon$ as functions of $T^*=k_BT/\epsilon$, $\rho^*=\rho\sigma^3$, and $\Lambda^*/2\pi=\hbar/\sigma\sqrt{\epsilon m}$. From Eqs. (5.2)–(5.4) the reduced potential energy per particles is, up to order $\hbar^4$,

$$\frac{\Phi^*}{N}=\frac{\Phi_0}{N}+\left[\frac{\Lambda^*}{2\pi}\right]^2\frac{\Phi_1}{N}+\left[\frac{\Lambda^*}{2\pi}\right]^4\frac{\Phi_2}{N} \ , \tag{7.4}$$

where

$$\Phi_0=\langle\Phi^*(\hat{x})\rangle_c \ , \tag{7.5}$$

$$\Phi_1=\langle\Phi^*(\hat{x})\chi_1^*(\hat{x})\rangle_c-\langle\Phi^*(\hat{x})\rangle_c\langle\chi_1^*(\hat{x})\rangle_c \ , \tag{7.6}$$

$$\Phi_2=\langle\Phi^*(\hat{x})\chi_2^*(\hat{x})\rangle_c-\langle\Phi^*(\hat{x})\rangle_c\langle\chi_2^*(\hat{x})\rangle_c -\Phi_1\langle\chi_1^*(\hat{x})\rangle_c \ . \tag{7.7}$$

Here χ_1^* and χ_2^* are still given by Eqs. (4.2) and (4.3) and (4.9) and (4.10), but now all the quantities are taken in reduced units.

Similarly, from Eqs. (5.7)–(5.9) we have, for K^*/N,

$$\frac{K^*}{N}=\frac{K_0}{N}+\left[\frac{\Lambda^*}{2\pi}\right]^2\frac{K_1}{N}+\left[\frac{\Lambda^*}{2\pi}\right]^4\frac{K_2}{N} \ , \tag{7.8}$$

where $K_0=(3N/2)T^*$ and

$$K_1=m\sigma^2\left[\left\langle\frac{\hat{p}^2}{2m}\chi_1(\hat{r},\hat{p})\right\rangle_\Gamma-\frac{3N}{2}k_BT\langle\chi_1(\hat{r},\hat{p})\rangle_\Gamma\right] \ , \tag{7.9}$$

$$K_2=m^2\sigma^4\epsilon\left[\left\langle\frac{\hat{p}^2}{2m}\chi_2(\hat{r},\hat{p})\right\rangle_\Gamma-\frac{3N}{2}k_BT\langle\chi_2(\hat{r},\hat{p})\rangle\Gamma -\frac{K_1}{m\sigma^2}\langle\chi_1(\hat{r},\hat{p})\rangle_\Gamma\right] \ . \tag{7.10}$$

If the integration over the $\hat{p}$ variables is carried out, expressions (7.9) and (7.10) reduce to

$$K_1=\frac{1}{24T^{*2}}\langle\Phi_i^*(\hat{x})\Phi_i^*(\hat{x})\rangle_c \ , \tag{7.11}$$

$$K_2=\frac{1}{128T^{*2}}\left[\tfrac{4}{15}\langle\Phi_{iijj}^*(\hat{x})\rangle_c-\frac{1}{T^*}[\tfrac{4}{9}\langle\Phi_{ii}^*(\hat{x})\Phi_{jj}^*(\hat{x})\rangle_c+\tfrac{4}{45}\langle\Phi_{ij}^*(\hat{x})\Phi_{ij}^*(\hat{x})\rangle_c+\tfrac{4}{15}\langle\Phi_i^*(\hat{x})\Phi_{ijj}^*(x)\rangle_c] +\frac{2}{9T^{*2}}\langle\Phi_{ii}^*(\hat{x})\Phi_j^*(\hat{x})\Phi_j^*(\hat{x})\rangle_c\right]-K_1\langle\chi_1^*(\hat{x})\rangle_c \ . \tag{7.12}$$

From Eqs. (7.4) and (7.8) we also have

$$\frac{E^*}{N}=\frac{1}{N}(K_0+\Phi_0)+\left[\frac{\Lambda^*}{2\pi}\right]^2\frac{1}{N}(K_1+\Phi_1) +\left[\frac{\Lambda^*}{2\pi}\right]^4\frac{1}{N}(K_2+\Phi_2) \ . \tag{7.13}$$

By means of the virial theorem the pressure can be written as

$$p^*=\tfrac{2}{3}\rho^*\frac{K^*}{N}-\tfrac{1}{3}\rho^*\frac{W^*}{N} \ , \tag{7.14}$$

where the reduced virial W^* is

$$\frac{W^*}{N}=\frac{1}{N\epsilon}\left\langle\underline{R}\cdot\frac{\partial}{\partial\underline{R}}\Phi(\underline{R})\right\rangle \ . \tag{7.15}$$

Also W^* can be written as a series expansion up to $\hbar^4$ similarly to Eq. (7.4) since the operator to which it corresponds is a function only of $\underline{R}$. In particular we have

$$\frac{W^*}{N}=\frac{W_0}{N}+\left[\frac{\Lambda^*}{2\pi}\right]^2\frac{W_1}{N}+\left[\frac{\Lambda^*}{2\pi}\right]^4\frac{W_2}{N} \ , \tag{7.16}$$

where

$$W_0=\langle W^*(\hat{x})\rangle_c \ , \tag{7.17}$$

$$W_1=\langle W^*(\hat{x})\chi_1^*(\hat{x})\rangle_c-\langle W^*(\hat{x})\rangle_c\langle\chi_1^*(\hat{x})\rangle_c \ , \tag{7.18}$$

$$W_2=\langle W^*(\hat{x})\chi_2^*(\hat{x})\rangle_c-\langle W^*(\hat{x})\rangle_c\langle\chi_2^*(\hat{x})\rangle_c -W_1\langle\chi_1^*(\hat{x})\rangle_c \ . \tag{7.19}$$

Therefore, from Eqs. (7.14), (7.16), and (7.8) the expansion for the reduced pressure is

$$\begin{aligned}p^*&=\frac{\rho^*}{N}\left[(\tfrac{2}{3}K_0-\tfrac{1}{3}W_0)+\left[\frac{\Lambda^*}{2\pi}\right]^2(\tfrac{2}{3}K_1-\tfrac{1}{3}W_1) +\left[\frac{\Lambda^*}{2\pi}\right]^4(\tfrac{2}{3}K_2-\tfrac{1}{3}W_2)\right]\\ &=p_0+\left[\frac{\Lambda^*}{2\pi}\right]^2p_1+\left[\frac{\Lambda^*}{2\pi}\right]^4p_2 \ .\end{aligned} \tag{7.20}$$

The reduced free energy per particle F^*/N is given by

$$\frac{F^*}{N}=-\frac{1}{N}T^*\ln Z \ . \tag{7.21}$$

TABLE II. Quantum corrections to the kinetic energy. K_0/N is the classical value, while K_1/N and K_2/N are the first and second corrections, respectively. In the last columns those value of $(\Lambda^*/2\pi)^2$ are given for which the second correction amounts to 30% and 50% of the first.

T^*	ρ^*	K_0/N	K_1/N	K_2/N	$[(\Lambda^*/2\pi)^2]_{30\%}$	$[(\Lambda^*/2\pi)^2]_{50\%}$
0.52	1.005	0.780	81.72			
1.35	0.964	2.026	49.44	2005	0.0074	0.0123
0.75	0.833	1.125	43.84	2106	0.0062	0.0104
0.98	0.694	1.468	25.36	373	0.0204	0.0340
1.35	0.694	2.026	21.84	229	0.0286	0.0477
1.15	0.61	1.726	18.53			
1.728	0.35	2.592	6.97	−14	0.149	0.249
3.035	0.35	4.552	5.30	−4.1	0.388	0.646
5.0	0.365	7.455	4.61			

By means of Eq. (3.21) this can also be written in the form

$$\frac{F^*}{N}=\frac{F_0}{N}+\left[\frac{\Lambda^*}{2\pi}\right]^2\frac{F_1}{N}+\left[\frac{\Lambda^*}{2\pi}\right]^4\frac{F_2}{N}\ , \tag{7.22}$$

where

$$\frac{F_0}{N}=-\frac{1}{N}T^*\ln\left[\left[\frac{mk_BT}{2\pi\hbar^2}\right]^{3N/2}Q_c\right]\ , \tag{7.23}$$

$$\frac{F_1}{N}=-\frac{1}{N}T^*\langle\chi_1^*(\hat{x})\rangle_c\ , \tag{7.24}$$

$$\frac{F_2}{N}=-\frac{1}{N}T^*[\langle\chi_2^*(\hat{x})\rangle_c-\tfrac{1}{2}\langle\chi_1^*(\hat{x})\rangle_c^2]\ . \tag{7.25}$$

The quantum corrections to the kinetic energy up to $\hbar^4$ have been calculated by means of Eqs. (7.8)–(7.12) and the results are reported in Table II. In order to evaluate the quantum-corrected quantity for a particular substance one has to evaluate $\Lambda^*/2\pi$ and make use of Eq. (7.8). The last column of Table II gives that value of $(\Lambda^*/2\pi)^2$ for which the second correction becomes equal to 30% and 50% of the first. This should give an idea of the range of Λ^* values for which the Wigner-Kirkwood expansion for the kinetic energy can be used safely up to the second order. We have evaluated some corrections for various substances by making use of the entries of Table II and the parameters given in Table III. The results are illustrated in Fig. 2 and show that the corrections may become quite large as compared to the classical values. The arrows in Fig. 2 show the shift in kinetic energy for argon (label *a*), neon (label *n*), deuterium (label *d*), hydrogen (label *h*), and helium (label *he*) provided the substance meets the convergence criterion explained above.

Table IV shows the results for the potential energy as calculated by Eqs. (7.4)–(7.7). The meaning of the symbols is similar to Table II. It is seen that, whenever the series is converging, the corrections are very small even for genuine quantum systems like H_2 and D_2.

Corrections to the pressure were calculated by means of Eqs. (7.16)–(7.20) and the results of the kinetic energy of Table II. The quantities so obtained are given in Table V while Fig. 3 shows, similarly to Fig. 2, how the pressure for various substances differs from the respective classical value. The continuous curves in Fig. 3 give the isotherms as derived from Ref. 16. Table VI reports the results for the free energy as calculated from Eqs. (7.24) and (7.25) while the values of the classical free energy F_0/N have been calculated from the equation of state given in Ref. 16.

VIII. QUANTUM CORRECTIONS TO THE RADIAL DISTRIBUTION FUNCTION

The quantum-mechanical expression for the pair distribution function $g(\vec{r})$ is

$$g(\vec{r})=\mathrm{Tr}[\underline{\rho}\,\underline{\Gamma}(\underline{\vec{R}})]=\langle\underline{\Gamma}(\underline{\vec{R}})\rangle\ , \tag{8.1}$$

where $\vec{r}$ is the generic three-dimensional space vector and the operator $\underline{\Gamma}(\underline{\vec{R}})$ (not to be confused with the symbol Γ denoting classical phase space in the previous sections) is defined as

$$\underline{\Gamma}(\underline{\vec{R}})=\frac{1}{N\rho}\sum_{i=1}^{N}\sum_{\substack{j=1\\(j\neq i)}}^{N}\delta(\underline{\vec{R}}+\underline{\vec{R}}_i-\underline{\vec{R}}_j) \tag{8.2}$$

TABLE III. Reduction parameters and reduced values of h for various simple systems. $(\Lambda^*/2\pi)^2$ is the coefficient which appears in the series expansions. N_A is Avogadro's number and $\Lambda^*=h/\sqrt{\epsilon m\sigma^2}$.

	He	H_2	D_2	Ne	Ar	Kr	Xe
$\epsilon/k_B(K)$ (Ref. 21)	10.2	36.7	36.7	35.8	119.8	166.7	225.3
σ (Å) (Ref. 21)	2.556	2.959	2.959	2.75	3.405	3.68	4.07
$M=mN_A(g)$	4.0	2.0	4.0	20.2	39.9	83.8	131.3
Λ^*	2.680	1.726	1.221	0.592	0.186	0.101	0.062
$\left[\frac{\Lambda^*}{2\pi}\right]^2$	0.182	0.0755	0.0377	0.008 87	0.000 875	0.000 256	0.000 099

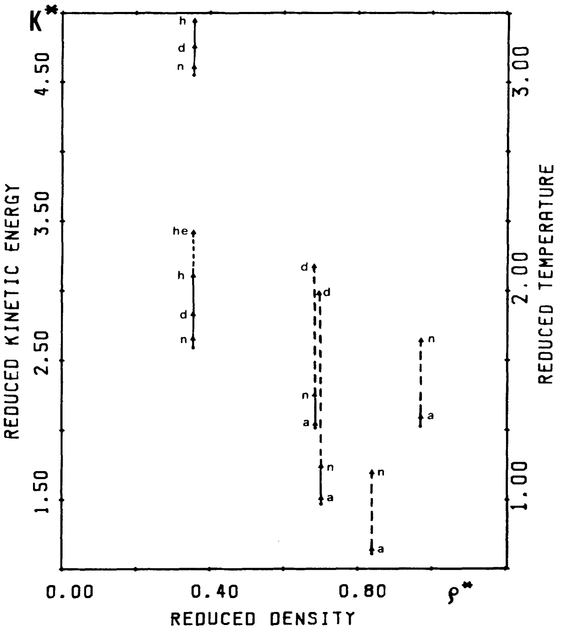

FIG. 2. Quantum corrections to the kinetic energy for various systems. The arrows show the change in reduced kinetic energy if corrections up to second order in $\hbar^2$ are taken into account. Solid arrows indicate that the convergence criterion (i.e., the second correction is smaller than 30% of the first) is fully satisfied, while broken arrows indicate that the second correction exceeds this limit but is still less than 50% of the first. The labels have the following meanings: *a*, argon; *n*, neon; *d*, deuterium; *h*, hydrogen; *he*, helium.

and $\underline{\vec{R}}$ is a generic three-dimensional space-vector operator. $\underline{\vec{R}}_i$ and $\underline{\vec{R}}_j$ are the position operators of particles *i* and *j*, respectively.

Since $\underline{\Gamma}$ is an operator which is a function only of space variables, Eq. (8.1) can be calculated by means of Eq. (2.7a) as

$$g(\vec{r})=\int d\hat{r}\,\rho_W(\hat{r})\frac{1}{N\rho}\sum_{i=1}^{N}\sum_{\substack{j=1\\(j\neq i)}}^{N}\delta(\vec{r}+\vec{r}_i-\vec{r}_j)\ , \qquad (8.3)$$

while the radial distribution function is

$$g(r)=\frac{1}{4\pi r^2}\int d\hat{r}\,\rho_W(\hat{r})\frac{1}{N\rho}\sum_{i=1}^{N}\sum_{\substack{j=1\\(j\neq i)}}^{N}\delta(r-r_j)\ , \qquad (8.4)$$

where $r=|\vec{r}\,|$. Using Eqs. (5.2)–(5.5) and (8.4) we thus have in reduced units $(x=r/\sigma)$

$$g(x)=g_0(x)+\left[\frac{\Lambda^*}{2\pi}\right]^2 g_1(x)+\left[\frac{\Lambda^*}{2\pi}\right]^4 g_2(x)+\left[\frac{\Lambda^*}{2\pi}\right]^6 g_3(x)\ , \qquad (8.5)$$

where

$$g_0(x)=\frac{1}{N\rho^*}\frac{1}{4\pi x^2}\left\langle\sum_{i=1}^{N}\sum_{\substack{j=1\\(j\neq i)}}^{N}\delta(x-x_{ij})\right\rangle_c\ , \qquad (8.6)$$

$$g_1(x)=\frac{1}{N\rho^*}\frac{1}{4\pi x^2}\left\langle\sum_{i=1}^{N}\sum_{\substack{j=1\\(j\neq i)}}^{N}\delta(x-x_{ij})\chi_1^*(\hat{x})\right\rangle_c - g_0(x)\langle\chi_1^*(\hat{x})\rangle_c\ , \qquad (8.7)$$

$$g_2(x)=\frac{1}{N\rho^*}\frac{1}{4\pi x^2}\left\langle\sum_{i=1}^{N}\sum_{\substack{j=1\\(j\neq i)}}^{N}\delta(x-x_{ij})\chi_2^*(\hat{x})\right\rangle_c - g_0(x)\langle\chi_2^*(\hat{x})\rangle_c - g_1(x)\langle\chi_1^*(\hat{x})\rangle_c\ , \qquad (8.8)$$

$$g_3(x)=\frac{1}{N\rho^*}\frac{1}{4\pi x^2}\left\langle\sum_{i=1}^{N}\sum_{\substack{j=1\\(j\neq i)}}^{N}\delta(x-x_{ij})\chi_3^*(\hat{x})\right\rangle_c - g_0^{(x)}\langle\chi_3^*(\hat{x})\rangle_c - g_1(x)\langle\chi_2^*(\hat{x})\rangle_c - g_2(x)\langle\chi_1^*(\hat{x})\rangle_c\ . \qquad (8.9)$$

The quantities (8.6)–(8.9) have been calculated for all the thermodynamic points reported in Table I, from the same

TABLE IV. Quantum corrections to the potential energy. Φ_0/N is the classical value, while Φ_1/N and Φ_2/N are the first and second corrections, respectively. In the last columns those values of $(\Lambda^*/2\pi)^2$ are given for which the second correction amounts to 30% and 50% of the first.

T^*	ρ^*	Φ_0/N (Ref. 22)	Φ_1/N	Φ_2/N	$[(\Lambda^*/2\pi)^2]_{30\%}$	$[(\Lambda^*/2\pi)^2]_{50\%}$
0.52	1.005	−7.716				
1.35	0.964	−5.851	14.61	−479	0.0092	0.0153
0.75	0.833	−5.990	12.95	−782	0.0050	0.0083
0.98	0.694	−4.850	8.84	−317	0.0084	0.0139
1.35	0.694	−4.618	7.32	−155	0.0142	0.0236
1.15	0.61	−4.179	6.90			
1.728	0.35	−2.282	3.85	−42	0.0275	0.0458
3.035	0.36	−2.014	2.06	−7.0	0.0883	0.147
5.0	0.365	−1.767				

TABLE V. Quantum corrections to the pressure. p_0 is the classical value, while p_1 and p_2 are the first and second corrections, respectively. In the last columns those values of $(\Lambda^*/2\pi^2)$ are given for which the second correction amounts to 30% and 50% of the first.

T^*	ρ^*	p_0 (Ref. 22)	p_1	p_2	$[(\Lambda^*/2\pi)^2]_{30\%}$	$[(\Lambda^*/2\pi)^2]_{50\%}$
0.50	1.005	−0.0792				
1.35	0.964	8.195	87.8	−563	0.0468	0.0780
0.75	0.833	0.0967	56.8	−835	0.0204	0.0340
0.98	0.694	−0.0914	21.5	−626	0.0103	0.0172
1.35	0.694	1.087	21.8	−280	0.0234	0.0389
1.151	0.61	0.061	13.0			
1.728	0.35	0.403	2.49	−20	0.0374	0.0623
3.035	0.35	1.268	2.27	−5.8	0.117	0.196
5.0	0.365	2.481				

simulations that were used for the thermodynamic properties, while the correction (8.7) has been obtained only for six of them, due to the excessive computer time needed in this case. These six points are the ones marked "RD" (rhombic-dodecahedral boundary conditions) in Table I.

The behavior of $g_1(x)$, $g_2(x)$, and $g_3(x)$ at all the thermodynamic points investigated is similar to that already reported in Refs. 4 and 5 and, for the sake of simplicity, it will not be displayed here again.[18] Instead we will give examples, at the various thermodynamic points, for the kind of convergence that can be obtained for various substances. In particular we report in the following figures the comparison between the classical and quantum mechanically corrected $g(x)$ up to the order $\hbar^6$, showing the cases with the highest value of Λ^* for which the series expansion (8.3) converges. The convergence criterion is equal to the one adopted previously for the thermodynamic properties.

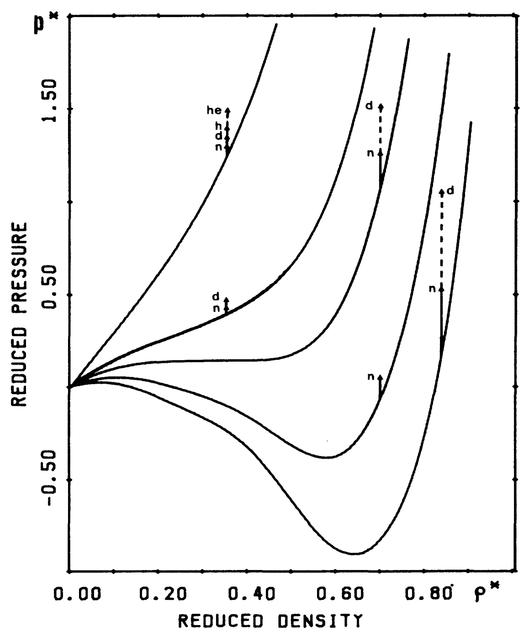

FIG. 3. Quantum corrections to the pressure for various systems. Solid lines show the classical values which were calculated from the equation of state given in Ref. 16. The reduced temperatures are, from top to bottom, 3.035, 1.728, 1.35, 0.98, and 0.75. The arrows again indicate the magnitude of the quantum corrections and have the same meaning and labels as in Fig. 2.

Figure 4 shows the classical $g_0(x)$ in the solid at $\rho^*=1.005$, $T^*=0.5$. At this point a satisfactory convergence of $g(x)$ was obtained only for the case of argon and it has not been reported in the figure because it does not differ appreciably from $g_0(x)$. Figure 5 shows the results for Ne at $\rho^*=0.833$, $T^*=0.75$ and $\rho^*=0.61$, $T^*=1.15$ while Fig. 6 still gives a comparison, again for Ne, of thermodynamic points which have either T^* or ρ^* in common, i.e., $\rho^*=0.964$, $T^*=1.35$; $\rho^*=0.694$, $T^*=1.35$; and $\rho^*=0.694$, $T^*=0.98$.

Figures 7 and 8 report the behavior of $g(x)$ for D_2 and H_2 at the thermodynamic points $\rho^*=0.35$, $T^*=1.7$; $\rho^*=0.35$, $T^*=3$; and $\rho^*=0.365$, $T^*=5$. The $g(x)$ for D_2 at $T^*=1.7$ and for H_2 at $T^*=1.7$ and $T^*=3$ were terminated at small x when the convergence of Eq. (8.3) was not satisfactory.

Figure 9, which we think is of particular interest, gives the $g(x)$ for He at $T^*=5$ and $\rho^*=0.365$, compared with the classical behavior and with the result of the calculation performed for the same system by Pollock and Ceperley with the path-integral Monte Carlo method.[6] The agreement between the two different methods of calculation is very good over the entire x region where the $\hbar$ series expansion converges satisfactorily and a comparison can be performed.

In the cases of He and H_2, at $T^*=5$, H_2 and D_2 at $T^*=3$, and at $T^*=1.7$, the convergence of the series (8.3) in the low x region has been improved by means of a (3,2) Padé approximant.

IX. CONCLUSIONS

We have calculated, by means of conventional molecular-dynamics computer simulations, for an N-body system of Boltzmann particles, the classical averages which determine the quantum corrections for a number of static properties. The particles were assumed to interact via a pairwise additive L-J potential. Simulations have been performed at nine different thermodynamic points in order to test the validity of the method over a wide range

TABLE VI. Quantum corrections to the free energy. F_0/N is the classical value, calculated from the equation of state of Ref. 16, while F_1/N and F_2/N are the first and second corrections, respectively. In the last columns those values of $(\Lambda^*/2\pi)^2$ are given for which the second correction becomes 30% and 50% of the first.

T^*	ρ^*	F_0/N	F_1/N	F_2/N	$[(\Lambda^*/2\pi)^2]_{30\%}$	$[(\Lambda^*/2\pi)^2]_{50\%}$
0.50	1.005		81.72	374	0.0655	0.109
1.35	0.964	−2.28	49.44	−100	0.148	0.247
0.75	0.833	−4.32	43.84	−199	0.0661	0.110
0.98	0.694	−3.95	25.36	−92.0	0.0827	0.138
1.35	0.694	−3.62	21.84	−52.9	0.124	0.206
1.15	0.61	−3.83	18.53	−58.0	0.096	0.160
1.728	0.35	−4.43	6.97	−18.8	0.111	0.185
3.035	0.35	−6.13	5.30	−6.43	0.247	0.412
5.0	0.365	−8.58	4.61	−3.00	0.461	0.768

of physical situations. Since quantum corrections calculated in this way are essentially fluctuations, carrying out such a program necessitated performing a total of approximately six million time steps, for systems with a number of particles ranging between 32 and 256. This has been possible because we had the opportunity of using freely, over a period of several months, the computer facilities of the Department of Physics of the University of Florence and of the Prozessrechenanlage Physik of the University of Vienna, during the unutilized time. Apart from eliminating spurious structures from $g(r)$, the use of different numbers of particles in the computation at most thermodynamic points has also demonstrated the independence of all the results on this variable.

The calculations of the quantum corrections to thermodynamical properties have shown that relatively large changes from the classical behavior can be computed with the Wigner-Kirkwood method within the convergence of the $\hbar$ expansion. The example of the quantum correction to the pressure is particularly striking. In fact, for Ne and D_2 at the reduced temperatures $T^*=0.75$, $T^*=0.98$, and $T^*=1.35$ the difference between the classical and the quantum-corrected behavior is quite large. It is also interesting to compare the predictions of our calculations with available experimental results for the equation of state. Table VII gives the comparison between the classical, quantum-corrected, and experimental values for the pressure of Ne at $\rho^*=0.69$, $T^*=0.98$ and for H_2 at $\rho^*=0.35$, $T^*=3$. The experimental results for Ne and H_2 are taken from Refs. 19 and 20, respectively. Even though in both cases the agreement between the calculation and the experimental results is still unsatisfactory, the

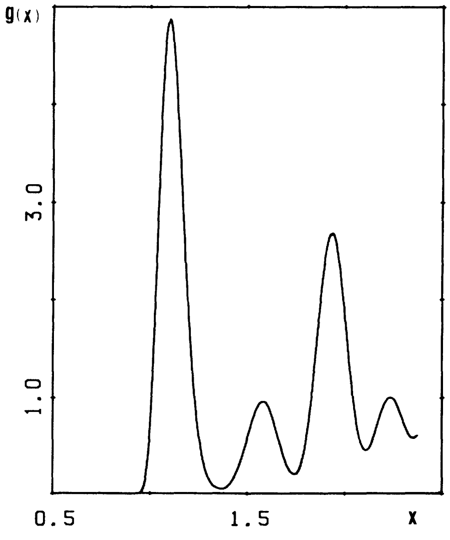

FIG. 4. Classical pair distribution function of a solid Lennard-Jones system at $\rho^*=1.005$, $T^*=0.52$. The quantum-corrected series is converging only for argon and the resulting $g(x)$ would be indistinguishable from the classical one on this scale.

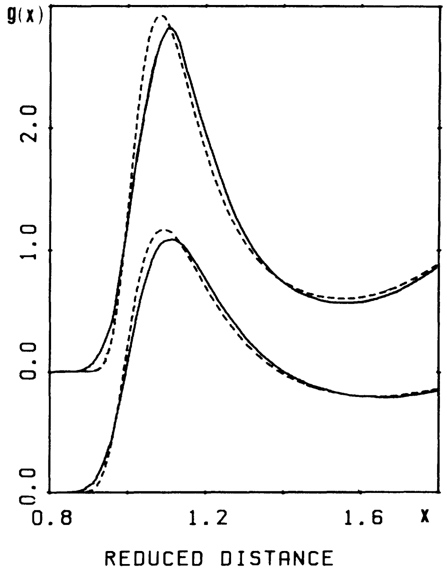

FIG. 5. Quantum corrections to the pair distribution function of Ne at $T^*=0.75$, $\rho^*=0.833$ (upper curves), and at $T^*=1.15$, $\rho^*=0.61$ (lower curves). The dashed lines are the classical results and the solid lines are the quantum-corrected ones up to the order $\hbar^6$.

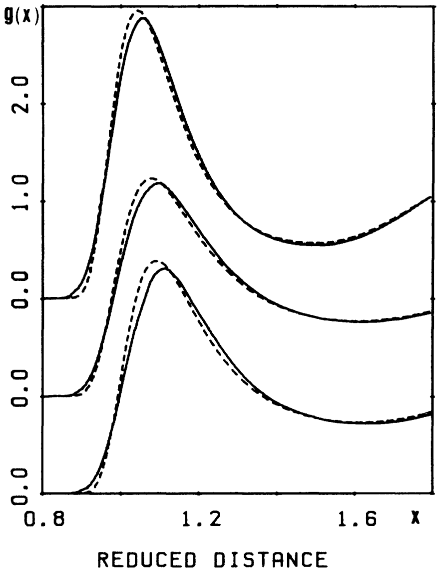

FIG. 6. Quantum corrections to the pair distribution function of Ne at $T^*=1.35$, $\rho^*=0.964$ (upper curves), at $T^*=1.35$, $\rho^*=0.694$ (middle curves), and at $T^*=0.978$, $\rho^*=0.694$ (lower curves). The dashed lines are the classical results and the solid lines are the quantum-corrected ones up to the order $\hbar^6$. Note that the first and the second are pertaining to the same temperature, while the second and third third are relative to the same density.

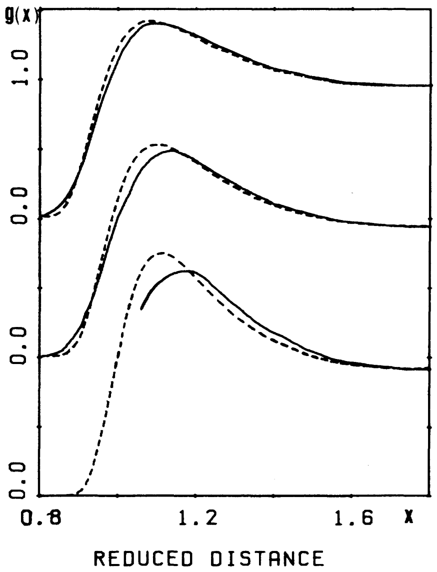

FIG. 7. Quantum corrections to the pair distribution function of D_2 at $T^*=5.0$, $\rho^*=0.365$ (upper curves), at $T^*=3.0$, $\rho^*=0.35$ (middle curves), and at $T^*=1.7$, $\rho^*=0.35$ (lower curves). The dashed lines are the classical results and the solid lines are the quantum-corrected ones up to the order $\hbar^6$. The lowest quantum-corrected curve has been terminated, at short distances, where the series expansion is not converging satisfactorily. The reduced density of 0.35 corresponds to the critical density for a classical Lennard-Jones system.

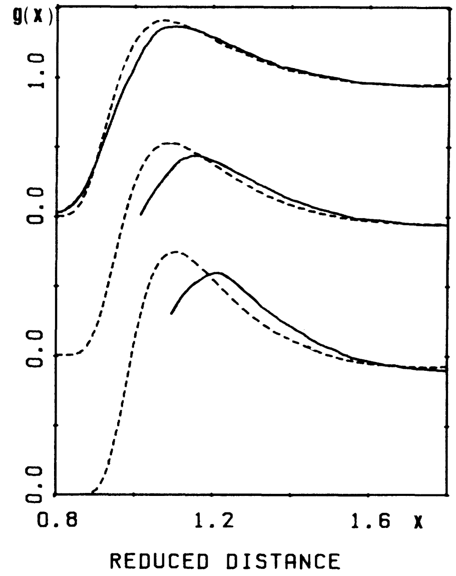

FIG. 8. Quantum corrections to the pair distribution function of H_2 at $T^*=5.0$, $\rho^*=0.365$ (upper curves), at $T^*=3.0$, $\rho^*=0.35$ (middle curves), and at $T^*=1.7$, $\rho^*=0.35$ (lower curves). The dashed lines are the classical results and the solid lines are the quantum-corrected ones up to the order $\hbar^6$. The two lowest quantum-corrected curves have been terminated, at short distances, where the series expansion is not converging satisfactorily.

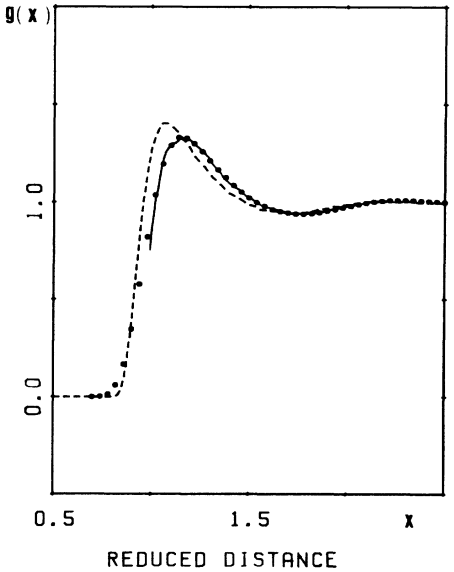

FIG. 9. Quantum corrections to the pair distribution function of He at $T^*=5.0$, $\rho^*=0.365$. The dashed line is the classical behavior while the solid line is the quantum-corrected one up to $\hbar^6$. This line has been terminated at short distances, where the series expansion is not converging any more. The dots are the path-integral Monte Carlo results of Pollock and Ceperley[6] for the same thermodynamic state. The agreement is excellent.

TABLE VII. Comparison of the calculated and experimental values of the pressure for Ne and H_2. p_0 is the classical result, p_{qc} is the quantum-corrected value up to the second order in $\hbar$. The experimental values are from Refs. 18 and 19. All pressures are given in atmospheres.

	T^*	ρ^*	p_0	p_{qc}	p_{exp}
Ne	0.98	0.694	−19.7	+10.8	21.4
H_2	3.035	0.35	248	275	287

improvement of the quantum-corrected values with respect to the classical ones can nevertheless be considered very good. This is particularly apparent for the case of Ne, for which the classical calculation gives an unstable situation while inclusion of some degree of quantum behavior greatly improves the result toward reality. Since the value of the pressure in dense systems is known to be very sensitive to the exact form of the interaction potential, most of the remaining disagreement between our calculation and the experimental results can be attributed to the use of the *L-J* potential instead of a more realistic potential.

The calculation of the quantum corrections to the radial distribution function has shown that the Wigner-Kirkwood method gives good results for Ne for all values of x at any thermodynamic point in the fluid. In a previous paper[5] these results have also been found to compare favorably with the available experimental data. For the case of more strongly quantum-mechanical systems like D, H, or He, the method offers the possibility of at least giving $g(x)$ down to values of $x \approx 1$, even when the difference from the classical behavior is quite large, although it is not possible to go below $T^* \approx 5$ for He and below $T^* \approx 1.7$ for H and D. Finally, the agreement of the two methods of calculation shown in Fig. 9 for the case of He at $T^* = 5.0$ strongly supports the validity of both.

APPENDIX

Here, in this Appendix, we will give the detailed expressions of the functions $\chi_2(\hat{r},\hat{p})$ and $\chi_3(\hat{r},\hat{p})$. The method is the same as the one used to derive $\chi_1(\hat{r},\hat{p})$ (Eq. 3.10). The functions will be expressed as polynomials in β; therefore, we have

$$\chi_2(\hat{r},\hat{p}) = \frac{1}{64m^2} \sum_{i=3}^{6} \beta^i \chi_2^{(i)}(\hat{r},\hat{p}) , \tag{A1}$$

where the coefficients of the various powers of β are

$$\chi_2^{(3)}(\hat{r},\hat{p}) = -\tfrac{1}{2}\Phi_{iijj} , \tag{A2}$$

$$\chi_2^{(4)}(\hat{r},\hat{p}) = \tfrac{1}{2}\Phi_{ii}\Phi_{jj} + \tfrac{1}{3}\Phi_{ij}\Phi_{ij} + \tfrac{2}{3}\Phi_i\Phi_{ijj} + \frac{1}{3m} p_j p_k \Phi_{iijk} , \tag{A3}$$

$$\begin{aligned}\chi_2^{(5)}(\hat{r},\hat{p}) = -\tfrac{1}{15}[&(1/2m^2) p_i p_j p_k p_l \Phi_{ijkl} + (5/m) p_j p_k \Phi_{ii}\Phi_{jk} + (4/m) p_i p_k \Phi_{ij}\Phi_{jk} \\ &+ (2/m) p_j p_k \Phi_i \Phi_{ijk} + 5\Phi_{ii}\Phi_j\Phi_j + 4\Phi_i\Phi_{ij}\Phi_j] ,\end{aligned} \tag{A4}$$

$$\chi_2^{(6)}(\hat{r},\hat{p}) = \tfrac{1}{18}[(1/m^2) p_i p_j p_k p_l \Phi_{ij}\Phi_{kl} + (2/m) p_k p_l \Phi_i\Phi_i\Phi_{kl} + \Phi_i\Phi_i\Phi_j\Phi_j] . \tag{A5}$$

Similarly,

$$\chi_3(\hat{r},\hat{p}) = \frac{1}{64m^3} \sum_{i=4}^{9} \beta^i \chi_3^{(i)}(\hat{r},\hat{p}) , \tag{A6}$$

where

$$\chi_3^{(4)}(\hat{r},\hat{p}) = -\tfrac{1}{48}\Phi_{iijjkk} , \tag{A7}$$

$$\chi_3^{(5)}(\hat{r},\hat{p}) = (1/48m) p_i p_j \Phi_{ijkkll} + \tfrac{1}{16}\Phi_{ii}\Phi_{jjkk} + \tfrac{1}{12}\Phi_{ij}\Phi_{ijkk} + \tfrac{1}{60}\Phi_{ijk}\Phi_{ijk} + \tfrac{1}{24}\Phi_{ijj}\Phi_{ikk} + \tfrac{1}{24}\Phi_{ijjkk}\Phi_i , \tag{A8}$$

$$\begin{aligned}\chi_3^{(6)}(\hat{r},\hat{p}) = -\tfrac{1}{6}[&(1/m^2) p_i p_j p_k p_l (\tfrac{1}{40}\Phi_{ijklmn}) \\ &+ (1/m) p_i p_j (\tfrac{1}{6}\Phi_{ijkl}\Phi_{kl} + \tfrac{2}{5}\Phi_{ikkl}\Phi_{lj} + \tfrac{1}{4}\Phi_{ijkk}\Phi_{ll} + \tfrac{1}{8}\Phi_{ij}\Phi_{kkll} + \tfrac{1}{10}\Phi_{ijk}\Phi_{kll} + \tfrac{1}{15}\Phi_{ikl}\Phi_{jkl} + \tfrac{1}{10}\Phi_{ijkkl}\Phi_l) \\ &+ (\tfrac{1}{4}\Phi_{ij}\Phi_{ij}\Phi_{kk} + \tfrac{2}{15}\Phi_{ij}\Phi_{jk}\Phi_{ik} + \tfrac{1}{8}\Phi_{ii}\Phi_{jj}\Phi_{kk} + \tfrac{1}{3}\Phi_{ijk}\Phi_{ij}\Phi_k + \tfrac{1}{2}\Phi_{iij}\Phi_j\Phi_{kk} \\ &\quad + \tfrac{2}{5}\Phi_{iij}\Phi_{jk}\Phi_k + \tfrac{1}{8}\Phi_{iijj}\Phi_k\Phi_k + \tfrac{1}{5}\Phi_{ijkk}\Phi_i\Phi_j)] ,\end{aligned} \tag{A9}$$

$$\begin{aligned}\chi_3^{(7)}(\hat{r},\hat{p}) = \tfrac{1}{7}[&(1/m^3) p_i p_j p_k p_l p_m p_n (\tfrac{1}{720}\Phi_{ijklmn}) \\ &+ (1/m^2) p_i p_j p_k p_l (\tfrac{4}{45}\Phi_{ijkm}\Phi_{ml} + \tfrac{7}{240}\Phi_{ijkl}\Phi_{mm} + \tfrac{7}{72}\Phi_{ijmm}\Phi_{kl} + \tfrac{1}{120}\Phi_{ijklm}\Phi_m + \tfrac{1}{72}\Phi_{ijm}\Phi_{klm}) \\ &+ (1/m) p_i p_j (\tfrac{7}{72}\Phi_{ij}\Phi_{kl}\Phi_{kl} + \tfrac{17}{90}\Phi_{ik}\Phi_{kl}\Phi_{lj} + \tfrac{7}{30}\Phi_{ik}\Phi_{kj}\Phi_{ll} + \tfrac{7}{48}\Phi_{ij}\Phi_{kk}\Phi_{ll} \\ &\quad + \tfrac{1}{5}\Phi_{ikl}\Phi_{jk}\Phi_l + \tfrac{7}{60}\Phi_{ijk}\Phi_k\Phi_{ll} + \tfrac{7}{36}\Phi_{ij}\Phi_k\Phi_{kll} + \tfrac{4}{45}\Phi_{ijk}\Phi_{kl}\Phi_l + \tfrac{7}{72}\Phi_{ijkk}\Phi_l\Phi_l + \tfrac{1}{30}\Phi_{ijkl}\Phi_k\Phi_l) \\ &+ (\tfrac{7}{72}\Phi_{ij}\Phi_{ij}\Phi_k\Phi_k + \tfrac{7}{48}\Phi_{ii}\Phi_{jj}\Phi_k\Phi_k + \tfrac{7}{30}\Phi_{ii}\Phi_j\Phi_{jk}\Phi_k + \tfrac{7}{36}\Phi_{ijj}\Phi_i\Phi_k\Phi_k + \tfrac{1}{15}\Phi_{ijk}\Phi_i\Phi_j\Phi_k + \tfrac{17}{90}\Phi_{ik}\Phi_{kj}\Phi_i\Phi_j)] ,\end{aligned} \tag{A10}$$

$$\begin{aligned}\chi_3^{(8)}(\hat{r},\hat{p}) = -(\tfrac{1}{8})[&(1/m^3)p_ip_jp_kp_lp_mp_n(\tfrac{1}{90}\Phi_{ij}\Phi_{klmn})\\ &+(1/m^2)p_ip_jp_kp_l(\tfrac{4}{45}\Phi_{ij}\Phi_{km}\Phi_{lm}+\tfrac{1}{18}\Phi_{ij}\Phi_{kl}\Phi_{mm}+\tfrac{2}{45}\Phi_{ijm}\Phi_m\Phi_{kl}+\tfrac{1}{90}\Phi_{ijkl}\Phi_m\Phi_m)\\ &+(1/m)p_ip_j(\tfrac{4}{45}\Phi_{ik}\Phi_{kj}\Phi_l\Phi_l+\tfrac{1}{9}\Phi_{ij}\Phi_k\Phi_k\Phi_{ll}\\ &\qquad+\tfrac{4}{45}\Phi_{ij}\Phi_k\Phi_{kl}\Phi_l+\tfrac{2}{45}\Phi_{ijk}\Phi_k\Phi_l\Phi_l)+(\tfrac{1}{18}\Phi_{ii}\Phi_j\Phi_j\Phi_k\Phi_k+\tfrac{4}{45}\Phi_{ij}\Phi_i\Phi_j\Phi_k\Phi_k)]\ , \qquad \text{(A11)}\end{aligned}$$

$$\begin{aligned}\chi_3^{(9)}(\hat{r},\hat{p}) = (\tfrac{1}{9})[&(1/m^3)p_ip_jp_kp_lp_mp_n(\tfrac{1}{144}\Phi_{ij}\Phi_{kl}\Phi_{mn})+(1/m^2)p_ip_jp_kp_l(\tfrac{1}{48}\Phi_{ij}\Phi_{kl}\Phi_m\Phi_m)\\ &+(1/m)p_ip_j(\tfrac{1}{48}\Phi_{ij}\Phi_k\Phi_k\Phi_l\Phi_l)+\tfrac{1}{144}\Phi_i\Phi_i\Phi_j\Phi_j\Phi_k\Phi_k]\ . \qquad \text{(A12)}\end{aligned}$$

Here we give also the functions $\chi_i(\hat{r})$ obtained averaging the $\chi_i(\hat{r},\hat{p})$ over the momentum space. Therefore, from Eqs. (3.10), (A1), and (A6) we obtain

$$\chi_1(\hat{r}) = \left[\frac{1}{24m}\right](\beta^3\langle\Phi_i\Phi_i\rangle - 2\beta^2\langle\Phi_{ii}\rangle)\ , \qquad \text{(A13)}$$

$$\chi_2(\hat{r}) = \left[\frac{1}{24m^2}\right]\sum_{i=3}^{6}\beta^i\chi_2^{(i)}(\hat{r})\ , \qquad \text{(A14)}$$

where

$$\chi_2^{(6)}(\hat{r}) = \tfrac{1}{48}\Phi_i\Phi_i\Phi_j\Phi_j\ , \qquad \text{(A15)}$$

$$\chi_2^{(5)}(\hat{r}) = -\tfrac{1}{10}\Phi_i\Phi_j\Phi_{ij}-\tfrac{1}{12}\Phi_i\Phi_i\Phi_{jj}\ , \qquad \text{(A16)}$$

$$\chi_2^{(4)}(\hat{r}) = \tfrac{1}{12}\Phi_{ii}\Phi_{jj}+\tfrac{1}{15}\Phi_{ij}\Phi_{ij}+\tfrac{1}{5}\Phi_i\Phi_{ijj}\ , \qquad \text{(A17)}$$

$$\chi_2^{(3)}(\hat{r}) = -\tfrac{1}{10}\Phi_{iijj}\ , \qquad \text{(A18)}$$

and, finally,

$$\chi_3(\hat{r}) = \left[\frac{1}{64m^3}\right]\sum_{i=4}^{9}\beta^i\chi_3^{(i)}(\hat{r})\ , \qquad \text{(A19)}$$

where

$$\chi_3^{(4)}(\hat{r}) = -\tfrac{1}{105}\Phi_{iijjkk}\ , \qquad \text{(A20)}$$

$$\begin{aligned}\chi_3^{(5)}(\hat{r}) = {}&\tfrac{1}{45}\Phi_{ii}\Phi_{jjkk}+\tfrac{4}{105}\Phi_{ij}\Phi_{ijkk}+\tfrac{1}{35}\Phi_{iijjk}\Phi_k+\tfrac{17}{630}\Phi_{iij}\Phi_{jkk}\\ &+\tfrac{1}{105}\Phi_{ijk}\Phi_{ijk}\ , \qquad \text{(A21)}\end{aligned}$$

$$\begin{aligned}\chi_3^{(6)}(\hat{r}) = {}&-\tfrac{1}{162}\Phi_{ii}\Phi_{jj}\Phi_{kk}-\tfrac{2}{135}\Phi_{ii}\Phi_{jk}\Phi_{jk}\\ &-\tfrac{32}{2835}\Phi_{ij}\Phi_{jk}\Phi_{ki}-\tfrac{2}{45}\Phi_{iij}\Phi_j\Phi_{kk}\\ &-\tfrac{4}{105}\Phi_{ijk}\Phi_{ij}\Phi_k-\tfrac{17}{315}\Phi_{iij}\Phi_{jk}\Phi_k\\ &-\tfrac{1}{90}\Phi_{iijj}\Phi_k\Phi_k-\tfrac{1}{35}\Phi_{iijk}\Phi_j\Phi_k\ , \qquad \text{(A22)}\end{aligned}$$

$$\begin{aligned}\chi_3^{(7)}(\hat{r}) = {}&\tfrac{1}{108}\Phi_{ii}\Phi_{jj}\Phi_k\Phi_k+\tfrac{1}{135}\Phi_{ij}\Phi_{ij}\Phi_k\Phi_k\\ &+\tfrac{1}{45}\Phi_{ii}\Phi_j\Phi_{jk}\Phi_k+\tfrac{1}{45}\Phi_{iij}\Phi_j\Phi_k\Phi_k\\ &+\tfrac{1}{105}\Phi_{ijk}\Phi_i\Phi_j\Phi_k+\tfrac{17}{630}\Phi_{ik}\Phi_{jk}\Phi_i\Phi_j\ , \qquad \text{(A23)}\end{aligned}$$

$$\chi_3^{(8)}(\hat{r}) = -\tfrac{1}{216}\Phi_{ii}\Phi_j\Phi_j\Phi_k\Phi_k-\tfrac{1}{90}\Phi_{ij}\Phi_i\Phi_j\Phi_k\Phi_k\ , \qquad \text{(A24)}$$

$$\chi_3^{(9)}(\hat{r}) = \tfrac{1}{1296}\Phi_i\Phi_i\Phi_j\Phi_j\Phi_k\Phi_k\ . \qquad \text{(A25)}$$

In fact, in order to perform the calculations of the various quantum corrections, it is useful to write $\langle\chi_i(\hat{r})\rangle_c=\langle\chi_i(\hat{r},\hat{p})\rangle_\Gamma=\langle\chi_i\rangle$ in a simplified form. This can be accomplished easily if we use, for any given function of the configuration space, $f(r)$, the following property:

$$\langle\Phi_i f(\hat{r})\rangle_c = (1/\beta)\langle f_i(\hat{r})\rangle_c\ . \qquad \text{(A26)}$$

Equation (A26) is obtained performing a partial integration and taking into account the fact that the potential must vanish at infinity. Therefore we end with

$$\langle\chi_1\rangle = -(\beta^2/24m)\langle\Phi_{ii}\rangle_c\ , \qquad \text{(A27)}$$

$$\langle\chi_2\rangle = \left[\frac{1}{144m^2}\right][(\beta^4/8)\langle\Phi_{ii}\Phi_{jj}\rangle_c+(\beta^4/20)\langle\Phi_{ij}\Phi_{ij}\rangle_c-(\beta^3/8)\langle\Phi_{iijj}\rangle_c] \qquad \text{(A28)}$$

$$\begin{aligned}\langle\chi_3\rangle = \left[\frac{1}{64m^3}\right]\{&\beta^6[-\tfrac{143}{10\,368}\langle\Phi_{ii}\Phi_{jj}\Phi_{kk}\rangle_c-\tfrac{113}{8640}\langle\Phi_{ii}\Phi_{jk}\Phi_{jk}\rangle_c-\tfrac{1}{2835}\langle\Phi_{ij}\Phi_{jk}\Phi_{ki}\rangle_c]\\ &+\beta^5[-\tfrac{1}{216}\langle\Phi_{iijj}\Phi_{kk}\rangle_c+\tfrac{17}{7560}\langle\Phi_{iijk}\Phi_{jk}\rangle_c-\tfrac{1}{90}\langle\Phi_{iij}\Phi_{jkk}\rangle_c+\tfrac{1}{5670}\langle\Phi_{ijk}\Phi_{ijk}\rangle_c]-\beta^4\tfrac{1}{567}\langle\Phi_{iijjkk}\rangle_c\}\ . \qquad \text{(A29)}\end{aligned}$$

With a derivation similar to those for $S_1(\hat{r})$ and $S_2(\hat{r})$ in Eqs. (4.9) and (4.10), we have, from Eq. (4.7),

$$S_3(\hat{r}) = \tfrac{1}{35}\sum_{4}^{7}\beta^i S_3^{(i)}(\hat{r})\ , \qquad \text{(A30)}$$

where

$$S_3^{(4)}(\hat{r}) = -\tfrac{1}{24}\Phi_{iijjkk}\ , \qquad \text{(A31)}$$

$$S_3^{(5)}(\hat{r}) = \tfrac{1}{8}\Phi_i\Phi_{ijjkk}+\tfrac{1}{6}\Phi_{ij}\Phi_{ijkk}+\tfrac{1}{24}\Phi_{ijk}\Phi_{ijk}+\tfrac{17}{144}\Phi_{ikk}\Phi_{ijj}\ , \qquad \text{(A32)}$$

$$\begin{aligned}S_3^{(6)}(\hat{r}) = {}&-\tfrac{4}{81}\Phi_{ik}\Phi_{kj}\Phi_{ji}-\tfrac{1}{8}\Phi_{ijkk}\Phi_i\Phi_j\\ &-\tfrac{1}{6}\Phi_{ijk}\Phi_{ij}\Phi_k-\tfrac{17}{72}\Phi_i\Phi_{ij}\Phi_{jkk}\ , \qquad \text{(A33)}\end{aligned}$$

$$S_3^{(7)}(\hat{r}) = \tfrac{1}{24}\Phi_{ijk}\Phi_i\Phi_j\Phi_k+\tfrac{17}{144}\Phi_{ik}\Phi_k\Phi_{ij}\Phi_j\ . \qquad \text{(A34)}$$

Since the derivation of the expressions for the $S_i(\hat{r})$ is independent of that for the $\chi_i(\hat{r})$, Eqs. (4.9)–(4.10) and (A30), have been used, together with (4.2)–(4.4), to verify the expressions (A13), (A14), and (A19).

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