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Pair distributions and energy-density functionals for liquid ^{4}He drops

Steven C. Pieper and R. B. Wiringa
Physics Division, Argonne National Laboratory, Argonne, Illinois 60439

V. R. Pandharipande
Department of Physics, University of Illinois, Urbana, Illinois 61801

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The pair-distribution function $g_2(\mathbf{r}_1,\mathbf{r}_2)$ in drops of liquid ^{4}He is studied with the variational Monte Carlo method. It is shown that in drops having 70 or more atoms it can be approximated as a functional of the local one-particle density and the separation r_{12}. Energy-density functionals based on this approximation of g_2 give a fairly accurate description of the ground-state properties of the drops.

The density-density correlation function, or the pair-distribution function, $g_2(\mathbf{r}_1,\mathbf{r}_2)$, of a many-body system containing A particles relates the joint probability $\rho_2(\mathbf{r}_1,\mathbf{r}_2)$ of finding two particles at $\mathbf{r}_1$ and $\mathbf{r}_2$ to the one-particle density $\rho_1(\mathbf{r})$ at $\mathbf{r}_1$ and $\mathbf{r}_2$:

$$\rho_2(\mathbf{r}_1,\mathbf{r}_2)=\rho_1(\mathbf{r}_1)\rho_1(\mathbf{r}_2)g_2(\mathbf{r}_1,\mathbf{r}_2) \quad . \tag{1}$$

In homogeneous liquids $(A\rightarrow\infty)$ $g_2(\rho_1,r_{12})$ is a function of the liquid density ρ_1 and the interparticle spacing $r_{12}=|\mathbf{r}_1-\mathbf{r}_2|$. In a spherically symmetric drop ρ_1 is a function of r and A, and the g_2 can depend upon A, r_1, r_2, and r_{12}.

We have studied $g_2(r_1,r_2,r_{12})$ in drops of liquid ^{4}He containing 8–240 atoms using the previously determined[1] variational Monte Carlo (VMC) wave function Ψ_v for the ground state. Comparisons[1,2] with exact Green's-function Monte Carlo (GFMC) calculations show that these and the related infinite-liquid variational wave functions give ground-state energies, single-particle densities, and a g_2 in liquid that are accurate within a few percent. Configurations of particle coordinates $\mathbf{r}_i$, $1\leq i\leq A$, were generated for each drop by sampling the $[\Psi_v(\mathbf{r}_i)]^2$ with the Metropolis Monte Carlo method. All pairs (i,j) in these configurations were binned according to the values of r_i, r_j, and r_{ij}. g_2 is obtained from the number of pairs in the bins; in the figures we give curves that result from smoothing the binned values.

There are two principal results of this study. First, the $g_2(r_1,r_2,r_{12})$ for each drop considered has no detectable dependence on r_1-r_2, and thus is a function of $R_m=(r_1+r_2)/2$ and r_{12} only. This feature is illustrated in Fig. 1 for the 112-atom drop. Second, for $A\geq 70$ g_2 for drops of different A depends mostly on $\rho(R_m)$ and r_{12}, whereas for $A\leq 40$ and small density there is an explicit A dependence. This result is shown in Fig. 2.

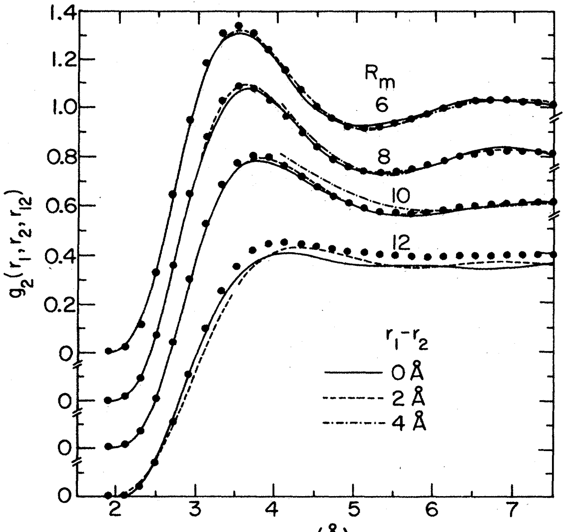

FIG. 1. $g_2(r_1,r_2,r_{12})$ for $A=112$ drop. The $R_m=6$, 8, and 10 sets have three curves each with $r_1-r_2=0$, 2, and 4 Å, while the $R_m=12$ set has only two curves with $r_1-r_2=0$ and 2. The statistical errors for the first three sets are $\sim\pm0.02$; for the $R_m=12$ set they are ±0.05. The dots give $g_{2,u}(\rho_1(R_m),r_{12})$.

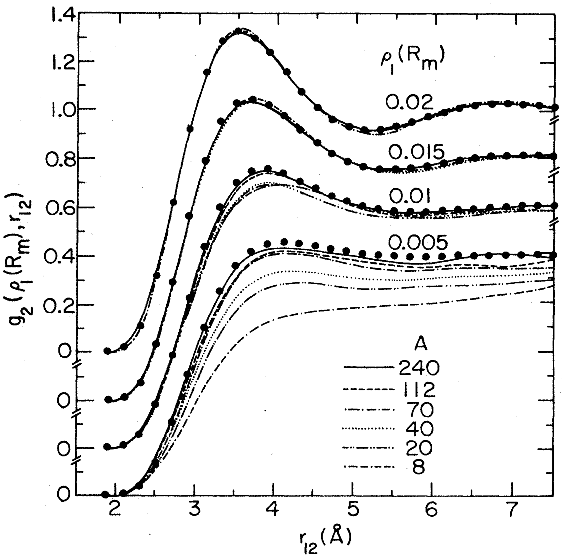

FIG. 2. $g_2(\rho_1(R_m),r_{12})$ for various drops. The $\rho_1=0.02$-Å^{-3} set has three curves for $A=240$, 112, and 70, the 0.015-Å^{-3} set has these and $A=40$, while the 0.01- and 0.005-Å^{-3} sets have six curves for drops of $A=240$, 112, 70, 40, 20, and 8. The statistical errors for the first three sets are $\sim\pm0.01$; for the 0.005-Å^{-3} set they are $\sim\pm0.03$. The dots give $g_{2,u}(\rho_1(R_m),r_{12})$.

The variational wave function of drops having $A \geqslant 20$ has the form

$$\Psi_v = \exp\left[\frac{1}{2}\left(\sum_i u_1(r_i) + \sum_{i<j} u_2(r_{ij}) + \sum_{i<j<k} u_3(r_{ij},r_{jk},r_{ki})\right)\right] . \tag{2}$$

The single-atom correlation $u_1(r)$ depends upon A; $u_2(r_{ij})$ has a weak (probably negligible) dependence upon A, while $u_3(r_{ij},r_{jk},r_{ki})$ has no significant dependence on A[1]. Manousakis and Usmani[3] have calculated $g_{2,u}(\rho_1,r_{12})$ in uniform liquid of density ρ_1, by setting $u_1=0$ in Eq. (2) and using the u_2 and u_3 found for the $A=112$ drop. They used the hypernetted chain method with the scaling approximation.[2] In principle these $g_{2,u}(\rho_1,r)$ are different from the $g_{2,L}(\rho_1,r)$ of the liquid. The latter exist only for those densities at which the liquid is stable, while $g_{2,u}$ are defined at all densities. At equilibrium density, $\rho_0=0.0219$ Å^{-3}, the $g_{2,u}$ and the GFMC $g_{2,L}$ are very close. The equilibrium energy and density of the uniform liquid obtained with this u_2 and u_3 are -6.74 K/A and $0.94\rho_0$, compared with -7.12 K/A and $0.99\rho_0$ obtained with the GFMC method.[4]

Figures 1 and 2 show that $g_2(\rho_1(R_m),r_{12})$ in the drops is very close to $g_{2,u}(\rho_1(R_m),r_{12})$ except at small ρ_1 and small A. The density distributions of the drops are very smooth; their surface thicknesses range from 5 to 7 Å. Consequently when $r_{12} < 5$ Å we have

$$\rho_1(R_m) \approx \rho_1(R_{\text{c.m.}}) \approx \tfrac{1}{2}[\rho_1(r_1)+\rho_1(r_2)]$$
$$\approx [\rho_1(r_1)\rho_1(r_2)]^{1/2} , \tag{3}$$

where $\mathbf{R}_{\text{c.m.}}$ is the center of mass $(\mathbf{r}_1+\mathbf{r}_2)/2$. On the other hand, g_2 does not have much density dependence for $r_{12} > 5$ Å. We have verified that for $A \geqslant 70$, within the errors indicated in Figs. 1 and 2,

$$g_2(r_1,r_2,r_{12}) \approx g_{2,u}(\hat{\rho}_1,r_{12}) , \tag{4}$$

where $\hat{\rho}_1$ is any of the average densities given in Eq. (3).

Krotscheck, Qian, and Kohn[5] have recently developed a theory of the inhomogeneous Bose system based on variational wave functions in which u_2 is a function of $\mathbf{r}_1$ and $\mathbf{r}_2$ and $u_3 \equiv 0$. They use the theory to study the surface of liquid ^{4}He, but due to various approximations their calculated surface tension is too small by a factor of 2. They criticize the present work in a note added in proof in Ref. 5, claiming that the near isotropy of our g_2 is a consequence of our assumption that u_2 is a function of r_{12} only. However, they find "anisotropy" in g_2 only at a very low density, $\rho_1=0.001$ Å^{-3} [see Figs. 5(a)-5(c) of Ref. 5] with their more general u_2. It is unclear whether this "anisotropy" is due to anything more than simple density variation in the presence of a surface, since they compare a $g_2(r_{12})$, where $\mathbf{r}_{12}$ is parallel to the surface and $\rho_1(R_m)$ is constant, to a $g_2(r_{12})$, where $\mathbf{r}_{12}$ is normal to the surface, $\mathbf{r}_1$ is fixed, and $\rho_1(R_m)$ continuously changes as r_{12} varies. If we plot our g_2 in an analogous manner, we also observe "anisotropic" behavior. The success of the VMC calculations based on $u_2(r_{12})$ in reproducing the GFMC binding energies, density profiles, and extrapolated surface tension[1] suggests that an isotropic u_2 is a good starting point for a variational wave function. The fact that approximation (4) is empirically satisfied is gratifying, but we do not believe it is a trivial consequence of the choice for u_2.

Chang and Cohen[6] have used approximation (4) to study the liquid surface. Following them we can express the energy of the A-body drop in terms of the n-particle densities $\rho_n(\mathbf{r}_1 \ldots \mathbf{r}_n)$. In particular, the energy given by the wave function (2) is obtained as

$$E = E_1 + E_2 + E_3 , \tag{5}$$

$$E_1 = E_{1,1} + E_{1,2} + E_{1,3} , \tag{6}$$

$$E_{1,1} = \frac{(A-1)}{A}\frac{\hbar^2}{8m}\int \nabla_1\rho_1(\mathbf{r})\cdot\nabla_1 \ln\rho_1(\mathbf{r})\,d\mathbf{r} , \tag{7}$$

$$E_{1,2} = -\frac{(A-1)}{A}\frac{\hbar^2}{8m}\int \rho_2(\mathbf{r}_1,\mathbf{r}_2)\nabla_1 u_2(r_{12})\cdot\nabla_1 \ln\rho_1(\mathbf{r}_1)\,d\mathbf{r}_1 d\mathbf{r}_2 , \tag{8}$$

$$E_{1,3} = -\frac{(A-1)}{A}\frac{\hbar^2}{16m}\int \rho_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\nabla_1 u_3(r_{12},r_{23},r_{31})\cdot\nabla_1 \ln\rho_1(\mathbf{r}_1)\,d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 , \tag{9}$$

$$E_2 = \frac{1}{2}\int \rho_2(\mathbf{r}_1,\mathbf{r}_2)\left[v(r_{12}) - \frac{\hbar^2}{4m}\nabla_1^2 u_2(r_{12})\right] d\mathbf{r}_1 d\mathbf{r}_2 , \tag{10}$$

$$E_3 = -\frac{\hbar^2}{16m}\int \rho_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\nabla_1^2 u_3(r_{12},r_{23},r_{31})\,d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 . \tag{11}$$

These equations are obtained by using the Jackson-Feenberg[7] kinetic energy and eliminating the $\nabla_1^2 u_1(r)$ term with the Born-Green-Yvon[6] identity:

$$\rho_1(\mathbf{r}_1)\nabla_1 u_1(r_1) = \nabla_1\rho_1(\mathbf{r}_1) - \int d\mathbf{r}_2\rho_2(\mathbf{r}_1,\mathbf{r}_2)\nabla_1 u_2(r_{12}) - \int d\mathbf{r}_2 d\mathbf{r}_3\rho_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\nabla_1 u_3(r_{12},r_{23},r_{31}) . \tag{12}$$

The $(A-1)/A$ factors in E_1 are obtained by subtracting the center-of-mass kinetic energy.

Hohenberg and Kohn[8] have shown that the ground-state energy of a many-body system is a universal functional of its $\rho_1(r)$. An approximate representation of this energy-density functional (EDF) for studies of drops and surfaces is obtained by using a local-density approximation (LDA) for ρ_2 and ρ_3 in Eqs. (8)-(11). g_2 is approximated with Eq. (4) (we use $\hat{\rho}_1 = \frac{1}{2}[\rho_1(r_1)+\rho_1(r_2)]$) and a plausible LDA for ρ_3 suggested by the hypernetted chain theory[2,9] is

TABLE I. Energies of liquid ^{4}He droplets in K/A.

A	VMC	EDF3	EDF3V	GFMC	EDF4	EDF4V
20	−1.57	−1.52	−1.53	−1.63	−1.58	−1.60
40	−2.39	−2.31	−2.35	−2.49	−2.45	−2.46
70	−3.03	−2.98	−2.99	−3.12	−3.13	−3.14
112	−3.50	−3.46	−3.49	−3.60	−3.65	−3.67
240	−4.19	−4.17	−4.19			−4.41
728	−4.95	−4.94	−4.98			−5.25

$$\rho_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=\rho_1(\mathbf{r}_1)\rho_1(\mathbf{r}_2)\rho_1(\mathbf{r}_3)g_2(\mathbf{r}_1,\mathbf{r}_2)g_2(\mathbf{r}_2,\mathbf{r}_3)g_2(\mathbf{r}_3,\mathbf{r}_1)\exp[u_3(r_{12},r_{23},r_{31})+A_{3,u}(\rho_{1m},r_{12},r_{23},r_{31})] \;, \tag{13}$$

where $A_{3,u}$ is the sum of Abe diagrams in uniform liquid at a mean density ρ_{1m}, which may be taken as the average of the $\rho_1(\mathbf{r}_i)$. Unfortunately, the integrals E_3 and $E_{1,3}$ are still difficult to evaluate numerically.

The VMC calculations for the 112-atom drop give $E_1=0.50$ K/A, $E_2=-4.07$ K/A, and $E_3=0.09$ K/A, while uniform-liquid calculations using the same u_2 and u_3 give $E_1=0$ K/A, $E_2=-6.75$ K/A, and $E_3=0.07$ K/A at $\rho=\rho_0$. Because E_3 is so small, it is reasonable to approximate it further as follows:

$$E_3\approx\int d\mathbf{r}E_{3,u}(\rho_1(\mathbf{r}))\rho_1(\mathbf{r}) \;, \tag{14}$$

where $E_{3,u}(\rho_1)$ is E_3/A in uniform liquid of density ρ_1. We define EDF3 to include $E_{1,1}$, $E_{1,2}$, and E_2 with the LDA Eq. (4), and E_3 with the LDA Eq. (14). It gives, when used with the VMC $\rho_1(r)$ for the 112-atom drop, $E_{1,1}=0.23$, $E_{1,2}=0.24$, $E_2=-4.04$, and $E_3=0.11$ K/A. The sum $E_{1,1}+E_{1,2}$ is very close to the exact E_1, so the neglect of the small $E_{1,3}$ is justified. The E_2 and E_3 from EDF3 are also quite close to the VMC values. The total energies obtained with EDF3 and VMC $\rho_1(r)$ for drops containing 20–728 atoms are given in Table I. EDF3 seems to be quite accurate in reproducing the VMC energies.

The $E(\rho_1)$ obtained for the uniform liquid with the present u_2 and u_3 differs from the GFMC $E(\rho_1)$ in the region $\rho_1=0.9\rho_0$–$1.2\rho_0$ by $\sim-0.42(\rho_1/\rho_0)^3$ K/A. We can take this difference into account by adding an E_4 term

$$E_4=-(0.42\text{ K})\int d\mathbf{r}[\rho_1(\mathbf{r})/\rho_0]^3\rho_1(\mathbf{r}) \tag{15}$$

to EDF3. The resulting functional is denoted by EDF4; when used with the GFMC $\rho_1(r)$, it gives energies, listed in Table I, that are very close to the GFMC energies.[1]

Both EDF3 and EDF4 can be used to calculate the energies and $\rho_1(r)$ in droplets by minimizing the energy with respect to variations in $\rho_1(r)$. To study the feasibility of such calculations, we parametrized the $\rho_1(r)$ as

$$\rho_1(r)=c/[1+\exp((r-R)/a)]^p \;, \tag{16}$$

and determined R, a, and p by minimizing the energy. The energies from this calculation are given in Table I, columns labeled EDF3V and EDF4V, and the densities are shown in Fig. 3. The calculated energies are very accurate, however, the surface thickness of the large drops is underestimated by $\sim 20\%$. We have also calculated the surface tension and thickness of a plane infinite surface. The calculated values with EDF4 (EDF3) are 0.269 (0.253) K Å^{-2} and 5.7 (5.8) Å. The experimental value for the tension is 0.274 K Å^{-2}. There are no direct measurements of the surface thickness. Earlier calculations of the surface properties with the EDF formalism have been reviewed by Edwards and Saam.[10]

Local-density approximations and EDF's are commonly used in nuclear physics to calculate properties of nuclei.[11] The phenomenological Skyrme[12] EDF is very popular, but has little direct connection with the bare interactions among the particles. The main advantage of the present EDF appears to be its inclusion of correlation effects and its direct connection with the microscopic Hamiltonian. Starting from the Brueckner-Bethe-Goldstone theory, Bethe, Negele, Siemens, and others have developed the LDA for effective interactions to be used in Hartree-Fock calculations.[13] That formalism has similarities with the present work. The $E_{1,1}$ term becomes the Hartree-Fock kinetic energy, and E_2 becomes the interaction energy. However, it appears that the analogue of $E_{1,2}$ has not been considered in that approach. Terms like $E_{1,2}$ are generally neglected in the EDF used to study many-electron systems.[14] We find that $E_{1,2}$ almost doubles the total E_1 and increases the surface thickness by 10–15%. It is amusing to note that we may absorb most of the effect of $E_{1,2}$ by calculating the $E_{1,1}$ with an effective mass of $\sim 0.5m$.

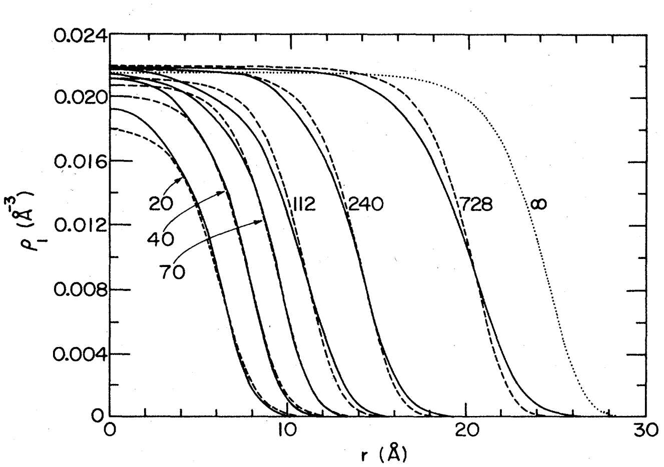

FIG. 3. The $\rho_1(r)$ in drops and the plane surface. The full lines show GFMC results for $A=20$, 40, 70, and 112 particles, and VMC results for $A=240$ and 728. The dashed lines give the EDF4V results. The dotted curve is the EDF4V surface plotted with its half-density point set arbitrarily at $r=24$ Å.

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[1] V. R. Pandharipande, J. G. Zabolitzky, S. C. Pieper, R. B. Wiringa, and U. Helmbrecht, Phys. Rev. Lett. **50**, 1676 (1983).

[2] Q. N. Usmani, S. Fantoni, and V. R. Pandharipande, Phys. Rev. B **26**, 6123 (1983).

[3] E. Manousakis and Q. N. Usmani (private communication).

[4] M. H. Kalos, M. A. Lee, P. A. Whitlock, and G. V. Chester, Phys. Rev. B **24**, 115 (1981).

[5] E. Krotscheck, G.-X. Qian, and W. Kohn, Phys. Rev. B **31**, 4245 (1985).

[6] C. C. Chang and M. Cohen, Phys. Rev. A **8**, 1930 (1973); **8**, 3131 (1973).

[7] H. W. Jackson and E. Feenberg, Ann. Phys. (N.Y.) **15**, 266 (1961).

[8] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[9] Q. N. Usmani, B. Friedman, and V. R. Pandharipande, Phys. Rev. B **25**, 4502 (1982).

[10] D. O. Edwards and W. F. Saam, Prog. Low Temp. Phys. **7A**, 283 (1978).

[11] J. W. Negele, Rev. Mod. Phys. **54**, 913 (1982).

[12] D. Vautherin and D. M. Brink, Phys. Lett. **32B**, 149 (1970); Phys. Rev. C **5**, 626 (1972).

[13] H. A. Bethe, Annu. Rev. Nucl. Part. Sci. **21**, 93 (1971).

[14] R. O. Jones, Phys. Rev. Lett. **52**, 2002 (1984).