

Variational Monte Carlo study of heavy-atom impurities in liquid ${}^4\text{He}$

K. E. Kürten

*Institut für Theoretische Physik, Universität zu Köln, 5000 Köln 41, West Germany
and Courant Institute of Mathematical Sciences, New York University, New York, New York 10012*

J. W. Clark

McDonnell Center for the Space Sciences and Department of Physics, Washington University, St. Louis, Missouri 63130

(Received 18 March 1985)

The static behavior of a single massive atomic impurity in bulk liquid ${}^4\text{He}$ is studied variationally, based on a Jastrow ground-state wave function for the host-impurity complex. Techniques are devised for efficient Monte Carlo integration of expectation values relating to the impurity, making possible accurate evaluation of the relevant chemical-potential difference, partial radial-distribution functions, and partial structure functions. Taking the specific examples of a single Xe or Cs impurity, we obtain extensive variational Monte Carlo results for these quantities, using approximately optimal Jastrow two-body pseudopotentials determined by paired-phonon analysis within a hypernetted-chain scheme. By virtue of the extremely different impurity-host potentials involved (essentially attractive versus essentially repulsive, respectively), the Xe and Cs examples are seen to represent opposite extremes in the nature of the structural disturbance of the host medium produced by the impurity. Concomitantly, the Monte Carlo simulations are much more strongly dependent on the particle number in the Cs impurity problem than for Xe. Parallel results for the chemical potential differences, radial-distribution functions, and structure functions have been obtained via the leading hypernetted-chain approximation, permitting some conclusions to be drawn regarding the accuracy of this approximation.

I. INTRODUCTION

During the last decade, our microscopic understanding of homogeneous systems of strongly interacting Bose and Fermi fluids has progressed rapidly, setting the stage for attacks on more challenging problems involving surfaces, interfaces, and finite clusters on the one hand and mixtures of different particle types on the other. An archetypal system which has some of the essential features of the broad class of inhomogeneous quantum systems and offers an intermediate step toward more complex examples is that of a single atomic or ionic impurity immersed in bulk liquid ${}^4\text{He}$.^{1,2} With regard to static properties, the characteristic spatial structure induced in the perturbed medium by the impurity is of particular interest³ and is susceptible to description within the existing microscopic models using associated calculational techniques. The dynamical properties of the impurity-helium system are already attracting experimental attention, most notably through studies of impacts of atomic Xe, Cs, etc. on large helium clusters.⁴ A microscopic account of such phenomena must await further practical development of many-particle theory.

In this paper we shall be concerned with the static, ground-state properties of a system consisting of a heavy atomic impurity, either Xe or Cs, embedded in liquid ${}^4\text{He}$. The calculational technique to be employed is the variational Monte Carlo procedure,⁵ tailored to the special circumstances produced by the foreign particle. The underlying theoretical superstructure is that of a binary boson mixture described by a two-component Jastrow wave

function,^{3,6,7} with correlations optimized (approximately) via paired-phonon analysis.⁸ For an asymptotically large host system, the impurity problem may be viewed as the small-concentration limit of such a boson mixture.

Parallel studies in which the impurity atom is either the mass-3 isotope of helium⁹ or various isotopes of hydrogen¹⁰ have recently been carried out and are being reported separately. Clearly, this set of investigations illuminates or anticipates existing or future variational treatments of the richer problems of heavy-atom-helium mixtures, ${}^3\text{He}$ - ${}^4\text{He}$ mixtures,^{11,12} and mixtures of hydrogen isotopes with bulk helium.¹³

In Sec. II we specify the problem addressed herein, state the basic assumptions of our description, and define the physical quantities—radial distribution functions, structure functions, and chemical potentials—of immediate relevance. In Sec. III we adapt the Monte Carlo scheme to the evaluation of these quantities. The results of extensive numerical calculations are summarized and discussed in Sec. IV.

II. PROBLEM FORMULATION

We consider a homogeneous system of $N-1$ identical background bosons of mass m_1 and one foreign particle of mass m_2 . It is imagined that both components are distributed uniformly within a cubic box of volume Ω , with overall particle density $\rho=N/\Omega$, this picture being repeated throughout all space by the imposition of periodic boundary conditions. The Hamiltonian of the system takes the form

$$H = -\frac{\hbar^2}{2m_1} \sum_{i=1}^{N-1} \Delta_i - \frac{\hbar^2}{2m_2} \Delta_N + \sum_{i < j}^{N-1} v_{11}(r_{ij}) + \sum_{k=1}^{N-1} v_{12}(r_{kN}), \quad (1)$$

into which one must substitute realistic interaction potentials v_{11} between two background particles and v_{12} between a background particle and the foreign atom.

We pursue a microscopic variational description in terms of a spatially correlated trial wave function of the Jastrow type:

$$\Psi = \exp \left[-\frac{1}{2} \sum_{i < j}^{N-1} u_{11}(r_{ij}) - \frac{1}{2} \sum_{k=1}^{N-1} u_{12}(r_{kN}) \right]. \quad (2)$$

The first exponential factor is a Jastrow wave function for the background $(N-1)$ -boson system, with two-body pseudopotential $u_{11}(r)$; the second exponential accounts for the dynamical correlations between the background atoms and the impurity via the pseudopotential $u_{12}(r)$. Such a wave function is suitable whether the impurity atom is a boson or a fermion, since a single representative of a given particle species experiences no exchange correlations.

One option for the specification of the pseudopotentials $u_{11}(r)$ and $u_{12}(r)$ is to assume reasonable analytic forms and determine their parameters by minimization of the energy expectation value

$$\langle H \rangle = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \quad (3)$$

The popular McMillan or Schiff-Verlet choice,

$$u_{1\gamma}(r) = (b_{1\gamma}/r)^5, \quad \gamma = 1, 2 \quad (4)$$

will be considered here.

Alternatively, and preferably, the $u_{1\gamma}$ may be obtained by functional minimization of the energy expectation value,

$$\frac{\delta}{\delta u_{1\gamma}} \left[\frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \right], \quad \gamma = 1, 2. \quad (5)$$

For our purposes this minimization is best accomplished through a paired-phonon analysis^{6,8} (PPA).

The next consideration is the calculational scheme for evaluating the multidimensional integrals involved in (3) and in the various spatial distribution functions.

(i) Hypernetted-chain methods have been adapted to this task within the broader setting of a homogeneous, binary boson mixture.^{3,6,7} The resulting formalism refers to the case of asymptotically large N , where $N = N_1 + N_2$ is the sum of the populations of the two Bose components, and ultimately to the thermodynamic limit, where N goes to infinity at fixed particle density ρ . Equations and quantities associated with the single-impurity problem addressed here are obtained by going to the limiting regime of low concentration $x \sim 0$, where x is the fraction N_2/N of impurity atoms present.

(ii) However, greater accuracy can be achieved, in practice as well as in principle, by implementing stochastic or Monte Carlo integrations⁵ of (3) and of the structure functions and generalized structure functions involved in (5).

For the impurity problem, the most salient physically measurable quantities are the chemical potentials of impurity and background particles (especially their difference, denoted here by μ), the volume coefficient α [obtained via the definition $\rho(p, x) = \rho(p, 0)(1 + \alpha x)^{-1}$ after a measurement of the density of a dilute mixture relative to the density of the pure host, at fixed pressure p], and the partial radial-distribution functions $g_{1\gamma}(r)$ together with their associated static structure functions $S_{1\gamma}(k)$, $\gamma = 1, 2$. The relevant spatial distribution functions are defined by

$$\rho_1 \rho_\gamma g_{1\gamma}(r_{12}) = \frac{\langle \Psi | \psi_1^\dagger(\mathbf{r}_1) \psi_\gamma^\dagger(\mathbf{r}_2) \psi_1(\mathbf{r}_1) \psi_\gamma(\mathbf{r}_2) | \Psi \rangle}{\langle \Psi | \Psi \rangle}, \quad \gamma = 1, 2 \quad (6)$$

wherein the ψ 's and ψ^\dagger 's are the usual destruction and creation operators for the indicated particle types at the indicated positions and $\rho_1 = (N-1)/\Omega$, $\rho_2 = 1/\Omega$. The relevant static structure functions are defined in terms of these distribution functions according to^{3,7}

$$S_{1\gamma}(k) = \delta_{1\gamma} + \rho \int [g_{1\gamma}(r) - 1] e^{ik \cdot r} d^3r, \quad \gamma = 1, 2 \quad (7)$$

where $\rho = \rho_1 + \rho_2$.

For an infinite system, the difference between the chemical potential μ_i of the impurity and the chemical potential μ_b of a host particle may be evaluated as the zero-concentration limit of the partial derivative of the energy expectation value per particle with respect to the concentration x of foreign particles:

$$\mu = \mu_i - \mu_b = \left[\frac{\partial \langle H \rangle / N}{\partial x} \right]_{x=0}. \quad (8)$$

For a finite number of particles one deals instead with the expression

$$\mu = \frac{E_i - E_b}{1/N}, \quad (9)$$

in which E_b is the energy expectation value per particle of N "background" helium atoms and E_i the energy expectation value per particle of $N-1$ ^4He atoms and one impurity atom. Thus, (8) is appropriate for a hypernetted-chain (HNC) integral-equation treatment, while (9) must be used in a Monte Carlo calculation.

The HNC approach has recently been applied to several interesting impurity problems, namely, (a) a single ^3He atom in bulk liquid ^4He (Refs. 3 and 14), (b) a heavy foreign atom (in particular, Xe and Cs) in liquid ^4He (Ref. 3), and (c) atomic and molecular hydrogen-isotope impurities in liquid ^4He (Ref. 10). We note that in problem (a) the impurity experiences the same interactions as the background particles, i.e., $v_{12} = v_{11}$, but has a somewhat different mass, while in problem (b) the impurity-host interaction is vastly different from the host-host interaction and the impurity and host atoms differ vastly in mass. Case (c) is intermediate. Some Monte Carlo results are also available for these problems.^{9,15,10} To date, Monte Carlo techniques have not been invoked in the determination of optimal pseudopotentials through the PPA procedure, nor in fixing the parameters of the McMillan choice of the $u_{1\gamma}$. This limited implementation is justi-

fied in part by the finding that, for correlations chosen by minimizing the energy within the HNC framework, the results of Monte Carlo evaluation of the chemical-potential difference, the partial radial-distribution functions, and other quantities are usually in good accord with the corresponding integral-equation results.

In this paper we describe in some detail a Monte Carlo treatment of the heavy-impurity problem (b). The calculations are based on the following choices of the potentials v_{11} and v_{12} . For the interaction between background ^4He atoms we adopt the well-documented Hartree-Fock-dispersion helium potential (HFDHE2) of Aziz *et al.*¹⁶ For the interaction between background atoms and the impurity we follow the lead of Buck¹⁷ and Gspann¹⁸ and use a Lennard-Jones form $v(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, in which the well-depth and range parameters are taken as $\epsilon = 25.18$ K, $\sigma = 3.697$ Å and $\epsilon = 1.34$ K, $\sigma = 6.896$ Å for Xe and Cs impurities, respectively. Monte Carlo results are reported for both examples. As in previous calculations, we rely on HNC-optimized pseudopotentials as input. Only one density is considered for the background medium, namely, the experimental saturation density $\rho_1 = 0.02185$ Å⁻³.

In more than one sense, these two examples, Xe and Cs, represent opposite extremes. The strong attraction of Xe for He acts to concentrate the density of He atoms in the vicinity of the Xe foreigner in rather dramatic fashion relative to the local ordering in the pure host. By contrast, the repulsive component of the Cs-He interaction is so overwhelming that a net enhancement of host atoms in the vicinity of the impurity is strongly discouraged; indeed, a Cs atom would be rapidly expelled from the interior of a drop of liquid ^4He . Another distinction appears on the technical, computational level, where we find that the Monte Carlo results for Xe display only a very modest dependence on the number N of particles used in the simulation, whereas in the case of Cs it is necessary to go to rather large values of N before convergence is achieved.

In the next section, the special conditions faced in a Monte Carlo treatment of the impurity problem are discussed. Two questions arise: (i) How does one reduce the statistical errors for quantities related to the impurity atom? (ii) Is it possible to calculate the chemical-potential difference μ within a reasonable statistical error? We have found adequate answers for (i), and the calculation called for in (ii) has been realized with results which are presented and discussed in Sec. IV.

III. MONTE CARLO PROCEDURE FOR THE HEAVY-IMPURITY PROBLEM

The standard Monte Carlo algorithm proposed by Metropolis, Rosenbluth, Rosenbluth, Teller, and Teller¹⁹ (MRRTT) for calculating the properties of classical statistical systems, provides an extremely powerful tool for computing the multidimensional integrals involved in quantum-fluid energy expectation values and distribution functions such as (3) and (6). The MRRTT algorithm is a biased random walk in configuration space. In the usual

implementation of this procedure within quantum many-body variational theory, each particle is moved, one after the other, to a new position chosen from a uniform distribution inside a cube of side length s . Any such move is either accepted or rejected, depending on the magnitude of the trial wave function Ψ_t at the new position R' compared to its magnitude at the old position R . Acceptance follows automatically if $|\Psi_t(R')|^2$ is greater than or equal to $|\Psi_t(R)|^2$; otherwise, acceptance occurs with a probability $|\Psi_t(R')|^2/|\Psi_t(R)|^2$. If the move is not accepted, the configuration is returned to R . We say that a single pass through the system has been completed if successive move attempts have been made individually for all of the particles, $i = 1, \dots, N$. It may be shown that under very general conditions, the points or configurations generated by the random walk have the asymptotic probability density $p(R) = |\Psi_t(R)|^2$ as the number of passes increases without limit. In other words, this $p(R)$ plays the role of an equilibrium distribution, which is reached if the random walk is allowed to proceed long enough.

Let $\{R_j, j = 1, \dots, M\}$ be a set of configurations generated in this fashion, and let $f(R)$ represent the local value, in the configuration R , of the quantity which is to be averaged. Then, according to the central limit theorem, the expectation value of the quantity at hand, in the given trial state, may be approximated by $M^{-1} \sum_{j=1}^M f(R_j)$ with a statistical error which is proportional to $1/\sqrt{M}$ for large M . In particular, the energy expectation value for a system with Hamiltonian H is to be computed from

$$\langle H \rangle = M^{-1} \sum_{j=1}^M \frac{H\Psi_t(R_j)}{\Psi_t(R_j)}. \quad (10)$$

A judicious formulation of the local energy appearing in the summand of (10) is provided by

$$\frac{H\Psi_t}{\Psi_t} = \sum_{i=1}^N (V_i + 2T_i - \mathbf{F}_i^2), \quad (11)$$

where, specializing to the impurity problem, we would have

$$T_i = \begin{cases} -\frac{\hbar^2}{4m_1} \Delta_i \ln \Psi, & i = 1, \dots, N-1 \\ -\frac{\hbar^2}{4m_2} \Delta_i \ln \Psi, & i = N \end{cases} \quad (12)$$

$$\mathbf{F}_i^2 = \begin{cases} \frac{\hbar^2}{2m_1} (\nabla_i \ln \Psi)^2, & i = 1, \dots, N-1 \\ \frac{\hbar^2}{2m_2} (\nabla_i \ln \Psi)^2, & i = N \end{cases}$$

and

$$V_i = \sum_{j (\neq i)}^{N-1} v_{11}(r_{ij}) + v_{12}(r_{iN}). \quad (13)$$

The partial radial-distribution functions $g_{11}(r)$ and $g_{12}(r)$ defined by (6) may be similarly evaluated as expectation values using the configurations generated by the random walk.

In general, the MRRTT algorithm is very simple to program and test and, with a reasonable expenditure of computer time, leads to accurate results for single-component quantum systems. However, for the impurity problem, direct application of this algorithm as described above would lead to unacceptably large statistical errors in quantities associated with the impurity atom. The reason is easy to see: In a given pass, one gathers $(N-1)(N-2)$ pieces of information about the (identical) ${}^4\text{He}$ particles, compared to only $2(N-1)$ about the impurity. Thus, we modify the algorithm as follows. A pass is redefined as a sequence of (attempted) moves of the background particles $i=1, 2, \dots, N-1$, in which each (attempted) move of a background particle is followed by an (attempted) move of the foreign atom N . This modification proves to be quite effective in reducing the statistical errors involved in evaluation of the quantities relating to the impurity, as is vividly demonstrated in Figs. 1 and 2 for the partial radial-distribution function $g_{12}(r)$ of Xe. (Another very efficient strategy for improving the statistics of impurity-quantity computation is to accord preferential treatment to the host atoms which are assigned positions near the impurity atom, i.e., make more frequent attempts to move them.)

An additional technical point should be aired, concerning the evaluation of the chemical-potential difference μ via Eq. (9). A straightforward analysis of the statistical error $\delta\mu$ associated with the Monte Carlo treatment of this quantity gives

$$\delta\mu = N[(\delta E_i)^2 + (\delta E_b)^2]^{1/2}, \quad (14)$$

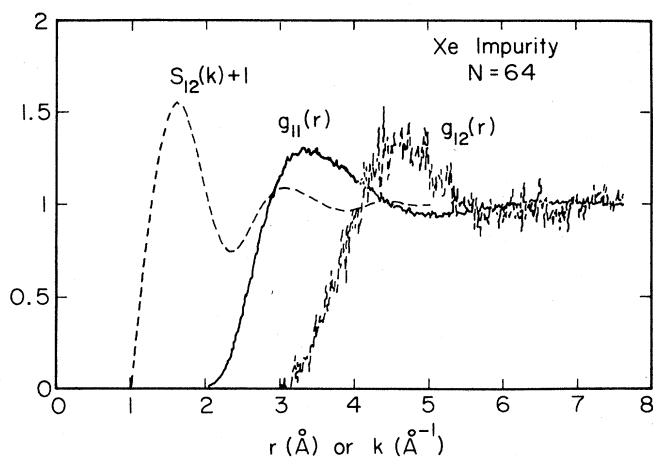


FIG. 1. Monte Carlo results for partial radial-distribution functions $g_{11}(r)$ and $g_{12}(r)$ and partial structure function $S_{12}(k)$ in the case of a Xe impurity in bulk ${}^4\text{He}$. A McMillan pseudopotential is assumed. Here and in all our calculations, the density of the host medium is taken at $\rho_1=0.02185 \text{ \AA}^{-3}$. The large scatter in the results for $g_{12}(r)$ is due to the direct application of the Metropolis, Rosenbluth, Rosenbluth, Teller, and Teller MRRTT algorithm, in which a move of the impurity atom is attempted once for every N attempted moves of the host particles.

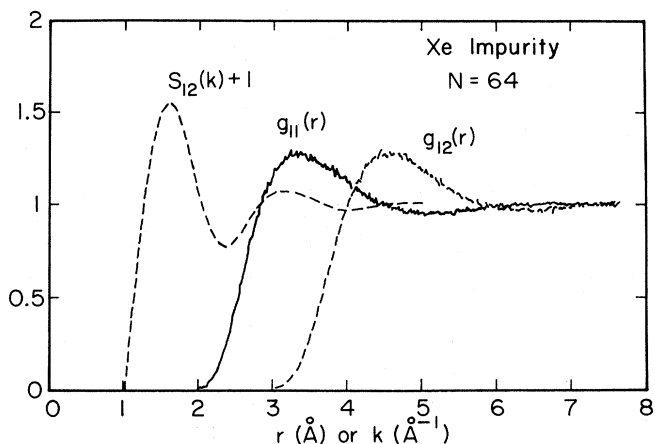


FIG. 2. Monte Carlo results for partial radial-distribution functions $g_{11}(r)$ and $g_{12}(r)$ and partial structure function $S_{12}(k)$ in the case of a Xe impurity in bulk ${}^4\text{He}$, based on a McMillan pseudopotential. Comparing with Fig. 1, the improved definition of the results for $g_{12}(r)$ is due to the use of a modified version of the MRRTT algorithm, in which each attempt to move a host particle is followed by an attempt to move the impurity.

wherein δE_i and δE_b are the absolute statistical errors in E_i and E_b , respectively. Thus, the relative statistical error in the difference of chemical potentials is

$$\frac{\delta\mu}{|\mu|} = \frac{[(\delta E_i)^2 + (\delta E_b)^2]^{1/2}}{|E_i - E_b|}. \quad (15)$$

Since the energy difference $E_i - E_b$ appearing in the denominator goes like $1/N$ for large N , the statistical error in μ may, in unfavorable cases, assume dangerously large values and may well be large compared to μ itself. This is particularly the case when $m_1 \simeq m_2$ and $v_{12} \simeq v_{11}$, as for a ${}^3\text{He}$ atom immersed in liquid ${}^4\text{He}$. There are several techniques which may be invoked to circumvent an unduly large statistical error in such cases; for example, (a) reweighting methods, (b) parametrization of the Hamiltonian, and (c) Baym's approximation. These techniques are detailed in Ref. 15. Baym's approximation²⁰ is especially simple: it rests on the assumption that the potentials v_{12} and v_{11} are identical and (within the present context) the *ansatz* that $u_{12} = u_{11}$. The chemical-potential difference then reduces to

$$\mu = T \left[\frac{m_1}{m_2} - 1 \right], \quad (16)$$

where T is the kinetic energy per particle of the pure background system.

Our primary concern in this paper is, however, the complementary situation in which the impurity atom has a considerably larger mass than the host particles and, importantly, the interactions v_{12} and v_{11} are substantially different. In this case, the denominator $|E_i - E_b|$ in (15) will ordinarily be large enough to allow us to realize a comfortably small statistical error in the evaluation of μ .

We may remark that although Baym's formula (16) may be generalized to the heavy-impurity problem by adding a term

$$\frac{\rho}{2} \int [(v_{12}(r) - v_{11}(r))g_{11}(r)]d^3r, \quad (17)$$

such an approximation is expected to be a rather poor one, since the pseudopotentials u_{12} and u_{11} must necessarily be allowed to differ significantly (resulting in significant differences between g_{12} and g_{11}), if the departure of v_{12} from v_{11} is to be realistically accounted for. Another relevant observation is that since a Xe or Cs impurity is some 30 times more massive than a ${}^4\text{He}$ background atom, the impurity is expected to behave essentially like a classical particle. (Of course, quantum mechanics must still be used to calculate the host-impurity radial distribution, since the ${}^4\text{He}$ host particles are definitely quantal in nature.) Thus, the physics of the problem addressed here will be different in important ways from that of the more extensively studied example of a ${}^3\text{He}$ atom in bulk ${}^4\text{He}$.

IV. NUMERICAL RESULTS AND DISCUSSION

A. Results for Xe

The numerical findings for the chemical-potential difference μ in the case of the Xe impurity are listed in Table I. Two choices of the pair of pseudopotentials u_{11}, u_{12} have been investigated, namely, (i) the McMillan choice with parameters b_{11} and b_{12} fixed through a HNC/0 treatment,³ and (ii) "optimal" correlations determined via PPA, again within the framework of the HNC/0 approximation. The Monte Carlo version (9) of μ appearing in the table was calculated for $N=64$, i.e., 63 ${}^4\text{He}$ atoms and one Xe impurity. To complete the technical picture we include values of the infinite-system version (8) of μ , obtained using the HNC/0 approximation. As in the Monte Carlo treatment of the pure ${}^4\text{He}$ system,²¹ the size dependence of the Monte Carlo estimate is rather weak: no substantial differences were observed between impurity systems with $N=32$ and $N=108$ particles.

In Fig. 3 we have a comparison of variational Monte Carlo and HNC/0 results for the radial-distribution function $g_{12}(r)$ and associated structure function $S_{12}(k)$, based on a McMillan choice of pseudopotentials. [Evidently some smoothing of the Monte Carlo $S_{12}(k)$ has been performed.] With the Monte Carlo calculation taken as a

TABLE I. Estimates of chemical-potential difference μ for the Xe impurity problem, based on McMillan (McM) and paired-phonon analysis—hypernetted-chain (PPA-HNC/0)—optimized correlations. Units are K. The statistical error accompanying the Monte Carlo value is computed from Eq. (14).

Estimate:	$N(E_i - E_b)$	$\partial(\langle H \rangle / N) / \partial x _{x=0}$
Method:	Monte Carlo	HNC/0
McM	-230.0 (± 5.5)	-212.5
PPA	-290.0 (± 7.0)	-287.0

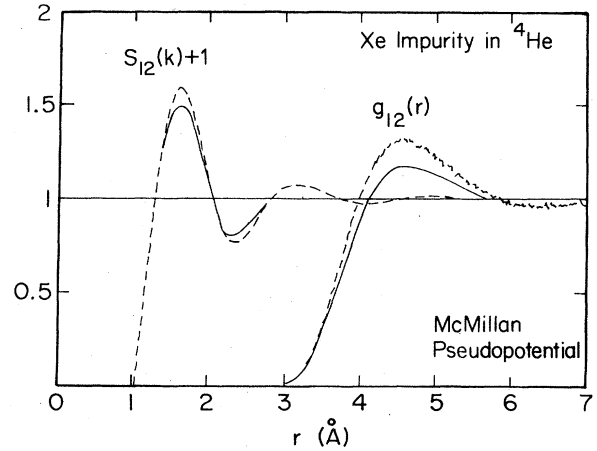


FIG. 3. Comparison of Monte Carlo (dashed or jagged curves) and HNC/0 (solid curves) results for the problem of a single Xe atom embedded in liquid ${}^4\text{He}$. The partial distribution function $g_{12}(r)$ and the partial structure function $S_{12}(k)$ are plotted against radial distance r and wave number k , respectively. A McMillan pseudopotential is assumed. The modified MRRTT algorithm was implemented in the Monte Carlo calculation, which refers to $N=64$ particles.

standard of accuracy, the HNC/0 evaluation is found to be significantly, though not grossly, in error. Figure 4 presents the same comparison for the PPA choice; in this case the HNC/0 procedure yields results in noticeably better agreement with Monte Carlo. Superimposing Figs. 3 and 4, we ascertain that the two choices of correlations lead to strikingly different results. In particular, the peaks of $g_{12}(r)$ and $S_{12}(k)$ are considerably higher in the PPA case. In truth, the Xe- ${}^4\text{He}$ impurity system is only crudely described by the McMillan *ansatz*, which is simply not flexible enough to take care of both the core and the large well depth which distinguish the Xe- ${}^4\text{He}$ interaction. For the McMillan pseudopotentials, the partial dis-

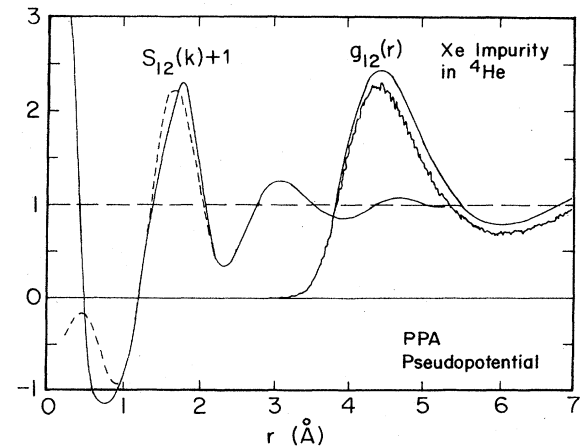


FIG. 4. Same as Fig. 3, except that a pseudopotential determined optimally within the PPA-HNC/0 scheme is assumed.

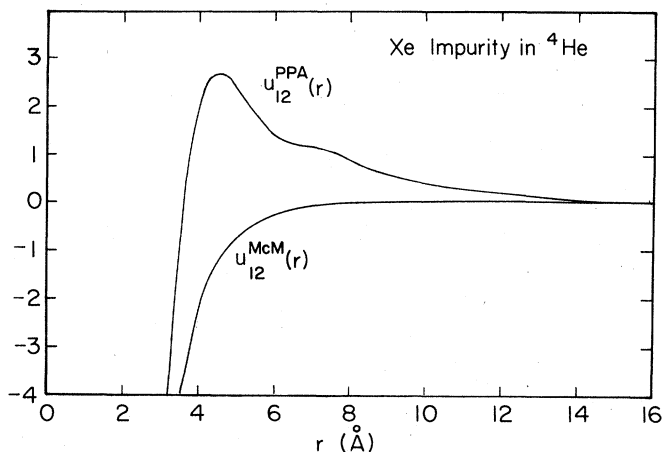


FIG. 5. Pseudopotential $u_{12}(r)$ for a Xe impurity in liquid ${}^4\text{He}$. The PPA curve is obtained by a paired-phonon analysis in the HNC/0 framework; a McMillan (McM) form is included for comparison.

tribution function $g_{12}(r)$ manifests no more structure than does the well-known distribution function $g_{11}(r)$ of the ${}^4\text{He}$ background, reflecting the fact that the parametrized form (4) is better suited to a potential with a dominant repulsive core than to the rapidly fluctuating v_{12} potential of the problem at hand. The inadequacy of the McMillan choice is also apparent from Table I: in the optimal PPA-HNC/0 case the energy is lower by about 25%.

These judgments regarding deficiency of the McMillan form are tempered by the fact that a rigorous optimization with respect to the parameters b_{11} and b_{12} was not attempted, in view of the obvious superiority of the PPA scheme. Rather, these parameters were determined by a minimization procedure based on Eqs. (24) and (25) of Ref. 3. However, Eq. (25) is predicated on fully optimal Jastrow correlations; there is otherwise an extra term in this formula which involves the derivative of g_{11} with respect to the density ρ . On the other hand, this term might well be small, since the term it corrects is not very large in the Xe case at hand (see Ref. 3). But even if it were large (which we suspect it to be in the Cs case considered below), that fact in itself would suggest that McMillan correlations depart in important ways from the optimal pseudopotentials.

The point has already been made in Ref. 3 that the strong oscillatory behavior of the “optimal” radial distribution function $g_{12}(r)$ (based on the PPA-HNC/0 pseudopotentials)—a behavior attributable to the immense attraction felt by the ${}^4\text{He}$ atoms outside the Xe- ${}^4\text{He}$ core—produces large-scale cancellations within and among the elementary diagrams neglected in the HNC/0 scheme. It is this feature which is responsible for the fact that the HNC/0 approximation suffers remarkably small errors, relative to the Monte Carlo evaluation, in the case of optimally determined Jastrow correlations. Referring to Table I, we observe that the HNC/0 result for μ misses the Monte Carlo result by only about 1%. As remarked above, the results for the mixed structure function $S_{12}(k)$ also agree quite well, except at smaller wave numbers where the disagreement may be ascribed (at least in part) to the finite box size of 15 Å for the 64 particles of the Monte Carlo treatment.

Physically, the prominent oscillations of the distribution function $g_{12}(r)$ in the optimal case correspond to a pronounced shell structure of the ${}^4\text{He}$ medium in the vicinity of the impurity. This accentuated shell structure, together with an associated strong initial peaking and subsequent modulation of the optimal pseudopotential $u_{12}(r)$ (displayed in Fig. 5), suggest that the simple Jastrow form does not faithfully imitate the correct ground-state wave function of the Xe- ${}^4\text{He}$ impurity system. It is estimated that there are some 14 He atoms in the first shell surrounding the Xe atom and hence there should exist significant angular correlations among the ${}^4\text{He}$ atoms near the impurity. However, one must look to a Green’s-function Monte Carlo treatment to establish the nature and the importance of such angular correlations in the exact ground state.

B. Results for Cs

Our numerical results in the case of a Cs impurity stand in marked contrast to those just reported for Xe. In the present case the host-impurity interaction has a very large repulsive core, surrounded by a very shallow attractive well. Consequently, the host particles tend to be ousted from the region of the impurity, rather than concentrated—as in the Xe case—toward the foreign par-

TABLE II. Estimates of chemical-potential difference μ for the Cs impurity problem (last two columns) and of the energy expectation value per particle E_i of one impurity atom and $(N-1)$ ${}^4\text{He}$ atoms, based on PPA-HNC/0—optimized correlations. Units are K. In the Monte Carlo case the value -5.95 ± 0.03 K is adopted for the energy expectation value per particle E_b of a system of N ${}^4\text{He}$ atoms. Over the range $N = 84-160$, this quantity shows little size dependence.

Estimate:	$E_i(N) \pm \delta E_i$	$N(E_i - E_b) \pm N[(\delta E_i)^2 + (\delta E_b)^2]^{1/2}$	$\partial(\langle H \rangle / N) / \partial x _{x=0}$
Method:	Monte Carlo	Monte Carlo	HNC/0
$N = 84$	-2.007 ± 0.056	331.2 ± 5.4	
$N = 120$	-3.874 ± 0.045	269.9 ± 7.0	
$N = 140$	-4.070 ± 0.047	263.2 ± 7.8	
$N = 150$	-4.286 ± 0.053	249.7 ± 9.1	
$N = 160$	-4.384 ± 0.052	250.6 ± 9.6	
$N = \infty$			

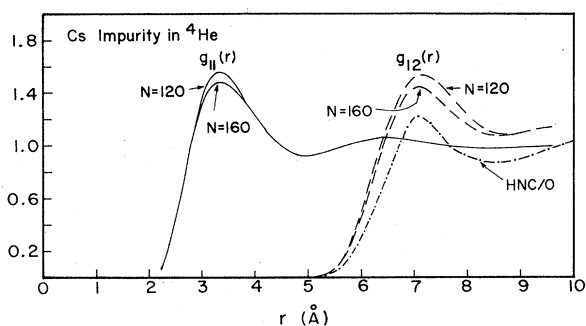


FIG. 6. Monte Carlo results for partial radial-distribution functions $g_{11}(r)$ and $g_{12}(r)$ in the case of a Cs impurity in liquid ${}^4\text{He}$, based on PPA-HNC/O optimal pseudopotentials. The substantial size dependence in this problem is illustrated by the difference between results at $N=120$ and at $N=160$, essential convergence having been reached by the latter value. The modified MRRTT algorithm was used. The HNC/O version of $g_{12}(r)$ (dot-dashed curve) is plotted for comparison.

ticle. In the present discussion we shall focus on results for the PPA-HNC/O-optimized pseudopotentials. (Calculations were also performed for McMillan correlations, optimized in an approximate fashion as described in Sec. IV A; however, the results are to be considered of technical value only.)

On examining Table II, which collects our principal results for the chemical-potential difference μ , two features are most conspicuous. First, the size dependence of the Monte Carlo estimate of μ is considerable; indeed, satisfactory convergence is not achieved until N reaches about 150. This contrasts with the very weak size dependence found in the Xe case. Secondly, the quantity μ takes on positive values, whereas it is negative in the case of a Xe impurity. A positive μ simply means that it costs more energy to remove a ${}^4\text{He}$ atom than to remove the Cs impurity; in reality the Cs atom would be propelled to the surface of a finite drop. Both features have their roots in the far more repulsive nature of the Cs-He interaction. We note that the size dependence is amplified because the extremely fat core of this interaction extends its influence further out than in, say, the Xe impurity problem and in other quantum-fluid problems studied previously. A

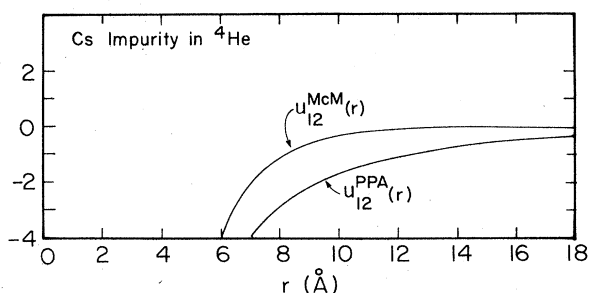


FIG. 7. Same as Fig. 5, but for a Cs impurity in the liquid- ${}^4\text{He}$ background.

third, more technical, conclusion to be drawn from Table II is that the HNC procedure for evaluation of energy expectation values is considerably less accurate than in the Xe case. Presumably this is due to the fact that the aforementioned large cancellations within and among the elementary diagrams, ascribable to strong oscillations of the distribution functions, especially $g_{12}(r)$, do not occur here. In comparison with the converged Monte Carlo result, the HNC/O approximation for μ is in error by about 10%. It should be mentioned that each Monte Carlo entry in Table II (as well as in Table I) represents an average of the results of 5–6 individual Monte Carlo runs of substantial length.

The absolute ratio $|\mu_T/\mu_V|$ of the kinetic and potential portions of the chemical-potential difference μ is a quantity of special physical interest. For the Cs problem we find a value 1.97 for this quantity, which may be somewhat of a surprise in view of our statement that Cs and Xe are essentially classical particles. However, it must be remembered that μ reflects the perturbation (modification in structure) of the background medium surrounding the impurity, and this disturbance (described, for instance, in terms of g_{12}) is certainly quantal, not classical. The much smaller value of $|\mu_T/\mu_V|$ found in the case of Xe, namely, 0.25, is in accord with our understanding of the difference in behavior of Cs and Xe impurities due to the different character of the relevant host-impurity interactions.

Figure 6 presents some Monte Carlo results for the partial radial-distribution functions. There are appreciable changes seen as we go from $N=120$ to $N=160$; however, at the latter particle number, the bulk-matter limit has been attained (except of course at large distances r). The converged $g_{12}(r)$ shows milder oscillations than are found in the Xe-impurity problem, as expected; moreover, we note the important property, alluded to above, that the peak of this distribution function lies much farther out in r than does the peak of the Xe-He distribution function.

Finally, the host-impurity pseudopotential for the Cs problem, as determined by the PPA-HNC/O prescription, is plotted in Fig. 7, with a McMillan form included for comparison. The bland behavior of the PPA result is in harmony with the relatively mild oscillations of the corresponding partial radial distribution $g_{12}(r)$. Again we find significant differences between the McMillan and PPA versions of $u_{12}(r)$, although (in contradistinction to the Xe case) their shapes are qualitatively similar.

ACKNOWLEDGMENTS

We thank G. V. Chester, J. Gspann, M. H. Kalos, M. D. Miller, M. L. Ristig, K. E. Schmidt, and P. A. Whitlock for information, advice, and fruitful discussions. We especially thank J. Gspann, who indicated to us the possibility of an opposite binding character of Xe and Cs impurities. This research was supported in part by the U.S. Department of Energy under Contract No. DE-AC02-76ER03077, by the National Science Foundation under Grant No. DMR-83-04213, and by the Deutsche Forschungsgemeinschaft under Grant No. Ri 267-7.

- ¹A. L. Fetter, in *The Physics of Liquid and Solid Helium*, edited by K. H. Bennemann and J. B. Ketterson (Wiley, New York, 1976).
- ²G. Baym and C. Pethick, in *The Physics of Liquid and Solid Helium*, Ref. 1.
- ³K. E. Kürten and M. L. Ristig, *Phys. Rev. B* **27**, 5479 (1983).
- ⁴J. Gspann and H. Vollmar, *J. Phys. (Paris) Colloq.* **39**, C6-330 (1978); J. Gspann, *Physica* **108B**, 1309 (1981); J. Gspann and R. Ries, *LT-17 (Contributed Papers)*, edited by U. Eckern, A. Schmid, W. Weber, and H. Wühl (Elsevier, Amsterdam, 1984); J. Gspann and R. Ries, *Surf. Sci.* (to be published).
- ⁵D. M. Ceperley and M. H. Kalos, in *Monte Carlo Methods in Statistical Physics*, edited by K. Binder (Springer, Berlin, 1979).
- ⁶K. E. Kürten and C. E. Campbell, *Phys. Rev. B* **26**, 124 (1982).
- ⁷K. E. Kürten and M. L. Ristig, *Nuovo Cimento* **2D**, 1057 (1983).
- ⁸C. E. Campbell and E. Feenberg, *Phys. Rev.* **188**, 396 (1969).
- ⁹K. E. Kürten and M. L. Ristig, *Phys. Rev. B* (to be published).
- ¹⁰K. E. Kürten and M. L. Ristig, *Phys. Rev. B* **31**, 1346 (1985).
- ¹¹J. C. Owen, *Phys. Rev. Lett.* **47**, 586 (1981).
- ¹²A. Fabrocini and A. Polls (unpublished).
- ¹³M. D. Miller, *Phys. Rev. B* **18**, 4730 (1978); M. D. Miller, *Ann. Phys. (N.Y.)* **127**, 367 (1980).
- ¹⁴A. Fabrocini and A. Polls, *Phys. Rev. B* **30**, 1200 (1984).
- ¹⁵K. E. Kürten, in *Recent Progress in Many-Body Theories*, edited by H. Kümmel and M. L. Ristig (Springer, Berlin, 1984).
- ¹⁶R. A. Aziz, V. P. S. Nain, J. S. Carley, W. L. Taylor, and G. T. McConville, *J. Chem. Phys.* **70**, 4330 (1979).
- ¹⁷W. Buck, *Adv. Chem. Phys.* **30**, 368 (1975).
- ¹⁸J. Gspann (private communication).
- ¹⁹M. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, G. H. Teller, and E. Teller, *J. Chem. Phys.* **21**, 1087 (1953).
- ²⁰G. Baym, *Phys. Rev. Lett.* **17**, 952 (1966).
- ²¹M. H. Kalos, M. A. Lee, P. A. Whitlock, and G. V. Chester, *Phys. Rev. B* **24**, 115 (1981).