Structure of Quantum Fluids at Nonzero Temperature*

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Abstract

A method is presented for the calculation of the structure of fluids and gases, such as He, Ne or H_2 , for which quantum effects are important. The method depends on finding an efficient Monte Carlo sampling technique to evaluate the appropriate averages which lead to the radial distribution function. The method is illustrated by results for the radial distribution function at finite temperatures and densities.

1. Introduction

The framework for a discussion of the properties of quantum fluids at nonzero temperatures is based on the determination of the quantum statistical density matrix. In configuration space this is the representation of the operator $e^{-\beta H}$, thus

$$\rho(x', x; \beta) = \langle x' \mid e^{-\beta H} \mid x \rangle, \tag{1}$$

where $x \equiv \{\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N\}$ and H is the *N*-particle Hamiltonian operator. This expression adequately takes account of the effects of quantum dynamics on the system, however in order to include the effect of quantum statistics it is necessary to ensure that only states with the proper Fermi or Bose statistics are included in the calculation of this matrix element. This can be done by calculating the properly symmetrised density matrix

$$\rho_{\text{sym}}(x,x';\beta) = \frac{1}{N!} \sum_{P} \delta_{P} \langle x' \mid e^{-\beta H} \mid Px \rangle, \qquad (2)$$

where the sum is taken over all permutation of the particles, Px representing a permutation of the coordinates and δ_P is the sign of the permutation (+1 for bosons and even permutations of fermions, -1 for odd permutations of fermions). The thermodynamic properties of the system can be derived from the quantum partition function Z, which is the trace of the density matrix, i.e.

$$Z = Tr(\rho_{\rm sym}). \tag{3}$$

* Dedicated to Professor Ian McCarthy on the occasion of his sixtieth birthday.

Thus the internal energy E is given by

$$E = -\frac{\partial \ell n Z}{\partial \beta} = \frac{Tr(H\rho_{\text{sym}})}{Tr(\rho_{\text{sym}})}.$$
 (4)

Path integrals (Feynman and Hibbs 1965) can be used to give an explicit representation of the density matrix and have proved to lead to successful numerical techniques for the calculation of the density matrix and associated statistical properties of various quantum systems. Some early calculations focussed on helium (Fosdick and Jordan 1966; Klemm and Storer 1973) and on Coulomb systems (Storer 1968) by treating the two-particle contributions. Later calculations attempted to treat many-particle systems (Zamalin and Norman 1973; Storer 1978; Barker 1979; Chandler and Wolynes 1981; Pollock and Ceperley 1984) and successfully included the effect of Bose statistics in the calculation (Ceperley and Pollock 1986). This paper will discuss some of the problems which arise from a naive attempt to carry out a Monte Carlo calculation of the path integrals involved and show how an approach based on effective potentials can improve dramatically the efficiency of the Monte Carlo process. We neglect the effect of Bose or Fermi statistics.

T (K)	λ/σ	Quantum effects
4	1.707	Dominant
16	0.855	
64	0-427	Some
256	0.213	
1024	0.107	Small

Table 1. Quantum effects over various temperature ranges

2. Path Integrals

One approach to the development of an expression for the path integral for the statistical density matrix (1) is to note the following relation

$$e^{-\beta H} = e^{-\beta H/M} e^{-\beta H/M} \dots e^{-\beta H/M}, \qquad (5)$$

which is exact for M factors and any values of M. This can be written in an approximate form by noting the following approximation

$$e^{-\beta H} \approx e^{-\beta V/2} e^{-\beta H_0} e^{-\beta V/2} + O(\beta^3)$$
(6)

which is valid at high temperatures (i.e. small β) for a Hamiltonian of the form $H = H_0 + V$. In order for this to be a good approximation we need the thermal de Broglie wavelength, λ , to be very much less than any characteristic size parameter of the system. For example, this is σ , the atomic diameter, for a simple fluid such as ⁴He. Indeed it is instructive to note for this case the various temperature ranges and the importance of the quantum effects: Table 1 illustrates this [note that $\lambda = (4\pi\hbar^2\beta/2m)^{\frac{1}{2}}$ and $\sigma \approx 2.556$ Å for ⁴He].

Equation (6) can be used when β is replaced by β/M , for any temperature, provided that M is large enough. Thus we are led to the approximation

$$e^{-\beta H} \approx e^{-\beta V/2M} e^{-\beta H_0/M} e^{-\beta V/M} \dots e^{-\beta H_0/M} e^{-\beta V/2M}.$$
(7)

If we neglect the effects of quantum statistics the trace of this quantity calculated in the configuration space representation gives a valid approximation to the partition function for the fluid, i.e.

$$Z = Tr(e^{-\beta H})$$

$$\approx \left(\frac{M}{\lambda^2}\right)^{\frac{3}{2}MN} \int \dots \int \exp\left[-\sum_{i=1}^{M} \sum_{j=1}^{N} \pi M(\mathbf{x}_j^{(i)} - \mathbf{x}_j^{(i+1)})^2 / \lambda^2 - \frac{\beta}{M} \sum_i \sum_{j < k} V(\mathbf{x}_{jk}^{(i)})\right] \prod_{i=1}^{M} d\mathbf{x}_1^{(i)} \dots d\mathbf{x}_N^{(i)}.$$
(8)

In the limit as $M \rightarrow \infty$ this expression is identical to the path integral representation of the partition function.

An approach that has been taken is to use a standard Metropolis sampling procedure to estimate the integral involved in (8) (or its derivatives), i.e. to shift a randomly chosen $\mathbf{x}_{j}^{(t)}$ by a distance $\boldsymbol{\delta}$ and accept or reject the move depending on the value of the integrand. There are two basic problems with this process. The first term in the expression (the Gaussian term) has a characteristic length scale equal to $\lambda/\sqrt{M\pi}$. The second term in the exponent (the potential term) has a characteristic length scale equal to σ . Since $\lambda/\sqrt{M\pi} \ll \sigma$ if M is large enough to ensure the validity of the approximation to the path integral, there is a basic mis-match in the length scales and the Metropolis procedure will be dominated by the first term in the exponential. Thus the sampling process may spend all the time trying to estimate the Gaussian integral form and it may require an abnormally long sequence to include fully the potential term. This is the basic reason for the large sampling errors involved in the early attempts at a Monte Carlo method for quantum systems. In addition the dimensionality of the integral in (8) is very large, being $3N \times M$. This could lead to an unacceptably long computing time.

To illustrate these points consider a calculation for ⁴He at, say, 4 K using 64 particles. If the high temperature approximation is taken at 1024 K, then M = 256 and the dimensionality of the integral is almost 50,000. This extremely high value, coupled with the fact that $\lambda/\sqrt{M\pi} \approx 0.15$ Å which is very much less than $\sigma \approx 2.5$ Å will make this approach unacceptable.

To resolve these problems one could first concentrate on the two-particle density matrix and find a much better approximation for $e^{-\beta H}$ than (6). Indeed, one can recognise that a better approximation to the two-particle density matrix is

$$e^{-\beta H} \approx e^{-\beta V_{\rm eff}/2} e^{-\beta H_0} e^{-\beta V_{\rm eff}/2} \tag{9}$$

with an appropriate choice of V_{eff} . The effective potential V_{eff} is a function of both r and the temperature and can be expressed in terms of the two-particle density matrix as

$$e^{-\beta V_{\text{eff}}(r;\beta)} = \lambda^6 \rho_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1, \mathbf{x}_2; \beta), \qquad (10)$$

which, of course, is an inversion of the configuration representation of (9). Whereas the approximation of (6) is only valid for ⁴He for temperatures much greater than 1024 K, the effective potential approximation (9) is valid for temperatures as low as 32 K.

The key to the successful use of this approximation is an accurate and computationally straightforward way of calculating the effective potential $V_{\text{eff}}(r;\beta)$. For this we can use the process initiated by Storer (1968) and Klemm and Storer (1973) which is based on the iterative scheme

$$e^{-2\beta H} = e^{-\beta H} e^{-\beta H}.$$
 (11)

which, in configuration space representation, can be written as

$$\rho_2(x',x;2\beta) = \int \rho_2(x',x'';\beta)\rho_2(x'',x;\beta)dx''.$$
 (12)

For two particles, we can start from the high temperature approximation (6) and use (12) to calculate the density matrix at 2β , i.e. half the temperature. This process can then be repeated to obtain the density matrix at half that temperature, and so on. To obtain the density matrix at 4 K starting from 1024 K would require only eight iterations. In practice the integral in (12), which is over the coordinates for two particles, can be reduced to a single radial integral and a sum over the relative angular momentum quantum number. This makes each angular momentum contribution, when the radial variable is discretised, appear as a 'matrix squaring' process with appropriate correction made near the large radius cut-off point.

To illustrate this result, the two-particle density matrix for ⁴He has been calculated at 32 K and (9) used to obtain the effective potential at this temperature. This is shown in Fig. 1 and compared with the basic Lennard-Jones potential. If this effective potential were used instead of the actual potential in (8) to calculate Z then

$$Z \approx \left(\frac{M}{\lambda^2}\right)^{\frac{1}{2}MN} \int \dots \int \exp\left[-\sum_{i=1}^M \sum_{j=1}^N \pi M(\mathbf{x}_j^{(i)} - \mathbf{x}_j^{(i+1)})^2 / \lambda^2 - \frac{\beta}{M} \sum_{i=1}^M \sum_{j < k} V_{\text{eff}}(x_{jk}^{(i)})\right] \prod_{i=1}^M d\mathbf{x}_1^{(i)} \dots d\mathbf{x}_N^{(i)}, \qquad (13)$$

only now to calculate the partition function for ⁴He at 4 K we only require M = 8. Thus not only is the dimensionality of the integrand reduced to the much more manageable 1536 but the value of $\lambda/\sqrt{M\pi} \approx 0.87$ Å, which measures the range of the Gaussian term, is much more compatible with the



Fig. 1. Effective potential for ⁴He at 32 K compared with the normal Lennard-Jones potential. Both potentials have been normalised by dividing by 32k, where k is Boltzmann's constant.

range $\sigma \approx 2.5$ Å of the potential term. There is still a gap between these two values which will lead to an unnecessarily long sequence of samples being used to essentially estimate the value of the Gaussian part of the integrand because of the relatively small values of the shift δ which are required. An alternative process which puts more emphasis on the potential term is described in the following section.

3. Alternative Monte Carlo Scheme

As an alternative to the above, one can use the properties of Gaussian functions which lead to multi-dimensional integrals which can be integrated analytically. We note, as a key to this method, that the classical partition function for a reference potential U(r) can be written in the following two alternative ways:

$$Z_{c} = \left(\frac{1}{\lambda^{2}}\right)^{\frac{3}{2}N} \int \dots \int \exp\left[-\beta \sum_{j < k} U(x_{jk})\right] d\mathbf{x}_{1} \dots d\mathbf{x}_{N}$$
(14)

or

$$Z_{c} = \left(\frac{M}{\lambda^{2}}\right)^{\frac{3}{2}MN} \int \dots \int \exp\left[-\sum_{i=1}^{M} \sum_{j=1}^{N} \pi M(\mathbf{x}_{j}^{(i)} - \mathbf{x}_{j}^{(i+1)})^{2} / \lambda^{2} -\beta \sum_{j < k} U(x_{jk}^{(1)})\right] \prod_{i=1}^{M} d\mathbf{x}_{1}^{(i)} \dots d\mathbf{x}_{N}^{(i)}.$$
(15)

The equivalence of these expressions can be verified by analytic integration of the Gaussian term over the variables $\mathbf{x}_{1}^{(i)}, \dots \mathbf{x}_{N}^{(i)}$ $(i = 2, \dots M)$.

Equation (13) differs from the second form by the replacement of the reference potential $U(x_{jk}^{(1)})$ by the average of the effective potential $\sum_{i=1}^{M} V_{\text{eff}}(x_{jk}^{(i)})/M$. The

ratio of the quantum partition function Z to the classical partition function Z_c is thus equal to

$$\frac{Z}{Z_c} = \left\langle \exp\left[-\frac{\beta}{M} \sum_{i} \sum_{j < k} V_{\text{eff}}(x_{jk}^{(i)}) + \beta \sum_{j < k} U(x_{jk}^{(1)})\right] \right\rangle.$$
(16)

Here the average is taken with respect to the normalised distribution:

$$\exp\left[-\sum_{i=1}^{M}\sum_{j (17)$$

The method then hinges on finding an efficient method for sampling from this distribution. We use an extension of the method used by Fosdick and Jordan (1966). The procedure is: first choose $\mathbf{x}_{j}^{(1)}(j=1...N)$ by using the Metropolis scheme, i.e. the points are chosen from the distribution $\exp[-\beta \Sigma_{j < k} U(x_{jk}^{(1)})]$. Secondly, for each sample choose $\mathbf{x}_{j}^{(i)}$ (i = 2,...M) recursively by

$$\mathbf{x}_{j}^{(i)} = \mathbf{x}_{j}^{(1)} \left(\frac{1}{M-i+2}\right) + x_{j}^{(i-1)} \left(\frac{M-i+1}{M-i+2}\right) + \lambda \boldsymbol{\xi} \sqrt{\frac{(M-i+1)}{4\pi(M-i+2)}},$$
(18)

where the components of the vector $\boldsymbol{\xi}$ are independent and normally distributed with a mean zero and a variance 1. This generates a closed chain of points with the Gaussian distribution of (17), with $\boldsymbol{x}_j^{(1)}$ being one point in the chain. In comparison with a classical Monte Carlo calculation this has the effect of replacing each particle position by a swarm of M particles with the size of the swarm being approximately λ , the thermal de Broglie wavelength. Provided that $\lambda \leq \sigma$ this provides an efficient method of sampling the distribution (17).

There is a certain amount of freedom in the choice of the reference potential U(r). In practice the most straightforward choice is to take U(r) to be V_{eff} multiplied by a constant factor. The factor is usually close to unity, however it should be chosen, or indeed U(r) should be chosen, to minimise the variance in the sampling of the average (16). This is often the case when $Z \approx Z_c$.

Since the calculation of the partition function is only an intermediate step in the determination of the thermodynamic properties of the system, it is more interesting to calculate other averages using the basic distribution. Foremost amongst these is the radial distribution function, g(r), which can be expressed as an average which involves a sum of δ -functions. Since a sample involving a δ -function is not practical in a finite number of steps we introduce the step function Δ defined by

$$\Delta(r-x) = \frac{1}{2\epsilon} \quad \text{when } x - \epsilon < r < x + \epsilon$$
$$= 0 \quad \text{elsewhere,} \tag{19}$$



Fig. 2. Radial distribution for ⁴He at 16 K for a density of (a) $n\sigma^3 = 0.1$, (b) $n\sigma^3 = 0.2$, and (c) $n\sigma^3 = 0.25$.



Fig. 3. Radial distribution function for neon at 33.78 K and a density of $n\sigma^3 = 0.2$ (dashed curve) compared with the classical two-particle contribution, $e^{-\beta V}$ (solid curve).

and write g(r) as

$$g(r) = \left\langle \sum_{i=1}^{M} \sum_{j < k} [\Delta(r - x_{jk}^{(i)})/M] \exp\left[-\frac{\beta}{M} \sum_{i} \sum_{j < k} V_{\text{eff}}(x_{jk}^{(i)}) + \beta \sum_{j < k} U(x_{jk}^{(1)}) \right] \right\rangle.$$
(20)

The parameter ϵ is chosen to be very much less than σ but large enough to iron out the fluctuations.

4. Results

A sample of results obtained using this method for ⁴He is presented in Fig. 2. The radial distribution function for ⁴He is shown for a range of densities, *n*, up to those for a dense gas. The dominant contribution for the case $n\sigma^3 = 0.1$ (Fig. 2*a*) is from two-particle effects. The quantum effect is quite strong here since the first peak would go to about 4.8 if the system was purely classical. The many-particle effects start to show up at higher densities with a suppression of g(r) for values of $r \sim 2\sigma$. These calculations were done with 32 particles; this number would have to be increased significantly to treat higher densities. The radial distribution function for neon is shown in Fig. 3 for T = 33.78 K above the boiling point. The comparison shown with the classical two-particle approximation indicates the effect of quantum dynamics for this moderately dense system. For this calculation only a modest value of M = 4 needed to be used along with the actual potential.

These promising results indicate that it is worthwhile to pursue more extensive computations at lower temperatures and to seek to include the effect of quantum statistics by an appropriate sampling of the permutations.

Acknowledgments

I am pleased to submit this paper as part of a tribute to Professor Ian McCarthy and thank him for his support over many years. I would also like to thank the Australian Research Council for their financial support.

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Manuscript received 7 December 1990, accepted 31 January 1991