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Fourier Path Integral Methods: A Model Study of Simple Fluids

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As illustrated by the diverse range of problems considered in the present volume, Monte Carlo based path-integral methods have widespread use in condensed-phase, many-body studies. The present note considers their use for the study of simple quantum fluids. In particular, we consider a model of a Lennard–Jones fluid for the purpose of examining the numerical convergence characteristics of a number of different path-integral approaches. The system chosen is liquid helium, which has been studied in detail by Pollock and Ceperley.(1)

As a primitive model of the numerical characteristics of this fluid we consider a one-dimensional "cage" of two fixed helium atoms separated by a distance of twice the reciprocal of the cube root of the fluid density. A third and movable helium atom is located within this cage and interacts with the other two atoms via a two-term Gaussian fit(2) to the helium Lennard–Jones potential ($\sigma = 2.556$ Å, $\varepsilon = 10.22$K). Using various path-integral methods described below, we then compute the free energy of this model system for various temperatures and note the relative convergence rates of the different methods.

Table I lists the free energy of our model system computed at two temperatures for a density of $\rho\sigma^3 = 0.365$. The free energies were computed using the "primitive" discretized method which iterates first-order estimates of the "short-time" density matrix.(3) The Trotter index, P, corresponds to the number of subintervals into which the interval $(0, \beta\hbar)$ is divided. The

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Table I. Free Energies[a] of the Present Model for a Reduced Density of 0.365 as Determined by the Primitive Discretized Path-Integral Method

$T = 51.1\text{K}$		$T = 5.11\text{K}$	
P	A/kT	P	A/kT
1	−0.85	1	−1.42
2	−0.81	2	−1.09
4	−0.80	4	−0.83
8	−0.79	8	−0.67
16	−0.79	16	−0.59
		32	−0.55
		64	−0.54
		128	−0.54
		256	−0.53

[a] In units of kT.

present calculations were done using the *NMM* method discussed by Thirumalai, Bruskin, and Berne.(4) The *NMM* method, especially useful for small-dimensional systems, gives free energy values (in units of kT) of −0.79 and −0.53 at $T = 51.1\text{K}$ and 5.11K, respectively. A measure of the magnitude of the quantum-mechanical effects can be obtained by recalling that the $P = 1$ values are the classical results.

Table II lists the corresponding free energies of the present model determined using Fourier path-integral techniques with and without "partial averaging;" see Ref. 5 for references. In the Fourier method the path integrals are performed by parameterizing the paths with a (truncated) Fourier series.(6) The path integration is thereby reduced to an integration over the Fourier coefficients, a procedure easily executed by numerical Monte Carlo methods. Partial averaging, described elsewhere in detail,(5,7) is an extension of this basic approach in which the effects of high-order Fourier coefficients (ignored in the basic method) are included (approximately) by means of a simple renormalization procedure. In its most elementary form this procedure replaces the "bare" potential by a Gaussian averaged one, the width of the Gaussian averaging reflecting both the thermal wavelength of the particle in question and the number of Fourier terms explicitly retained in the expansion of the paths. The linear combination of Gaussians used for the pair potentials was chosen to simplify the required Gaussian transformations.

Table II[a]

$T=51.1$K	$k_{\max}$	A/kT	A^{PA}/kT
	1	−0.84	−0.79
	2	−0.82	−0.79
	4	−0.80	−0.79
	8	−0.80	−0.79
	16	−0.79	−0.79
$T=5.11$K			
	1	−1.23	0.12
	2	−1.05	−0.22
	4	−0.89	−0.43
	8	−0.75	−0.50
	16	−0.66	−0.52
	32	−0.60	−0.53

[a] As in Table 1 except that the free energies are computed using the Fourier method with (PA) and without partial averaging. The parameter $k_{\max}$ is the number of explicit Fourier coefficients retrained in the description of the paths. Monte Carlo errors are less than or equal to 0.002 in all cases.

Consideration of Tables I and II indicates several conclusions. Most importantly, all methods studied do in fact converge to a common (presumably exact) free energy for the present model. As seen elsewhere,(7) the relative order of convergence of the free energy for the three methods considered is best for the partial average method, intermediate for the *NMM* procedure, and worst for the direct Fourier approach. It should be noted that the detailed rates of convergence of the various methods is, in general, a function of the thermodynamic property in question. From Table II we see that the partial averaging procedure significantly improves the convergence of the Fourier method. Indications of the present model study are, for example, that explicit Fourier coefficients of order 16 will be required to reach convergence for the 5.11K thermodynamic state of Pollock and Ceperley.(1) Preliminary results of liquid helium studies indicate that the above conclusions are correct and that the present model is in fact a useful one in estimating the convergence properties of various path-integral methods for problems of this type. Details of these calculations will be published elsewhere.(8)

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