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Monte Carlo calculation of the free energy for a dense fluid

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Abstract. In this paper, a simple and direct approach to the free energy of a dense simple fluid away from critical point is considered. Standard Monte Carlo sampling of free energy difference relative to a reference system for a range of model system sizes is employed. By using a range of a small number of particles, multi-stage samplings can be avoided and exponential extrapolation to the thermodynamic limit is assured in the absence of nearby critical point. The technique is demonstrated for the dense fluid interacting with the r^{-12} repulsive potential in three dimensions. The hard-sphere fluid reference system is used. The free energy estimate is in excellent agreement with published results from standard thermodynamic integration of the equation of state obtained from Monte Carlo simulation.

In the study of thermodynamic properties of dense fluids, it is important that one can calculate free energy efficiently (for a review, see Allen and Tildesley 1987). There are three approaches. The first is to use various integral equations or thermodynamic perturbation theories (for reviews, see Hansen and McDonald 1976, Barker and Henderson 1976). These methods are efficient and yield results in the thermodynamic limits, but are approximate. The second approach is computer simulation using molecular dynamic or Monte Carlo simulations (Allen and Tildesley 1987, Binder 1979). This approach is computationally intensive and yields the free energy with the aid of thermodynamic integration (Binder 1979). Such a method produces numerically exact estimates for a finite number of particles and often large number of particles are used to give good estimates for the thermodynamic limit. The third approach makes use of the Monte Carlo sampling of free energy differences between a reference system and the model system of interests (Valleau and Torrie 1977). This group also includes sampling of chemical potentials with the test particle method (for a review, see Widom 1982, Shing and Gubbins 1982). For systems with a large number of particles, multi-stage sampling (Valleau and Torrie 1977) is needed and the method becomes computationally demanding.

One direct and simple solution to this difficulty is to use a small number of particles and avoid the need for multi-stage sampling. The thermodynamic limit is then obtained by extrapolation of data for a range of system sizes. In the absence of a nearby critical point, there are no diverging length scales and the approach to the thermodynamic limit for a system with periodic boundary conditions is known to be exponential in the system sizes. (For a discussion of the exponential convergence, see Barber 1983.) Although these techniques seem to be very reasonable and straightforward, implementation for dense fluid model systems appears to be absent in the literature. In this paper, we provide such a contribution by considering the dense fluid interacting with the r^{-12} repulsive potential in three dimensions, where r is the separation between particles.

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The hard-sphere fluid references system is used and the extrapolated free energy is in excellent agreement with published results from standard thermodynamic integration of the equation of state obtained from Monte Carlo simulation (Hansen 1970, Hoover *et al* 1970).

A system of N_p classical point particles in a cubic box of volume V is considered with standard periodic boundary condition. The temperature is set by choosing $\varepsilon/k_B T = 1$ and the particles interact with the repulsive $v(r) = \varepsilon r^{-12}$ potential with a cutoff at $r = 2.0$. At the number density of $\rho = 0.8485$ used in this study, the tail correction due to the cutoff is 0.002, which is negligible when compared with expected estimated excess free energy per particle of $f/k_B T = 4.253$ (Hansen 1970). The reference system is the hard-sphere fluids at the same number density but with a hard-sphere diameter d, which is related to the packing fraction $\eta = \pi d^3 \rho/6$. The hard-sphere potential is denoted as v_0. The free-energy density difference relative to the free energy of the hard-sphere liquids $f_L(\eta)$ for $L^3 = N_p$ particles can be given (Mon 1985, Valleau and Torrie 1977) as

$$\delta f_L/k_B T \equiv (f_L^v - f_L(\eta))/k_B T = (1/N_p) \ln(\langle e^{-(v_0 - v)/k_B T} \rangle_v). \tag{1}$$

The ensemble average $(\langle\ \rangle_v)$ is performed in the model system (v) of interests. η is taken to be a parameter chosen to minimize the entropy density difference between the model system and the reference system for maximum sampling efficiency (Mon 1985). If N_p is not large, this ensemble average can be evaluated without multi-stage sampling (Mon 1985, Valleau and Torrie 1977). Since there are no second-order phase transitions or critical point in the r^{-12} and the hard-sphere fluids system (for review, see Hansen and McDonald 1976), the convergence in size is expected to be exponential in L (i.e. $\sim e^{-BL}$). In principle, there will be two different constants (B_v, B_η) describing the rate of convergence for the model and hard-sphere system. But in the large L limit, only the smaller (B) of the two are relevant. Then, the difference of the free-energy density converges as $e^{-BL}[1 - c\, e^{-\delta BL}] \sim e^{-BL}$ for $[1 - c\, e^{-\delta BL}] \sim$ constant: c is some constant and $\delta B = |B_v - B_\eta|$. $f_L^v - f_L(\eta)/k_B T$ is sampled according to equation (1) for

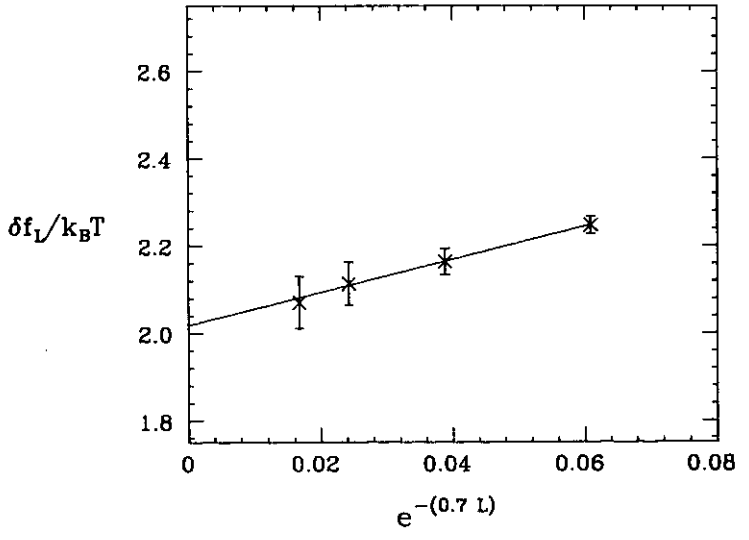

Figure 1. Finite size dependence of $\delta f_L/k_B T$ against e^{-BL} for $B = 0.7$. See equation (1) in text. The full line is a fit to the data.

a range of L and extrapolated to the large L limit. Finally, f_∞^v/k_BT can be estimated by using $f_\infty(\eta)/k_BT$ from the Carnhan–Starling free-energy density for the hard-sphere fluids (Carnahan and Starling, 1969, 1970).

We consider a sequence of system sizes with $N_p = 64$, 100, 150 and 200. Standard Monte Carlo sampling (for a review, see Binder 1979) is used with $\leqslant 10^5$ Monte Carlo moves per particle after equilibrium. Error estimates are obtained from using typically four different runs. The optimum value of η was found to be 0.33. An e^{-BL} dependence was assumed for $\delta f_L/k_BT$ and $B = 0.7$ was found to provide a good fit (see figure 1). The extrapolated value is 2.017 ± 0.06 and f_∞^v is obtained as 4.23 ± 0.06, in good agreement with 4.253 obtained from equation (17) of Hansen (1970). A value of $f_\infty(\eta = 0.33)/k_BT = 2.212\,74$ was taken from Carnahan and Starling (1969, 1970).

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