

Surface entropy of liquids via a direct Monte Carlo approach: Application to liquid Si

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(Received 16 January 1990)

We present two methods for a *direct* Monte Carlo evaluation of the surface entropy S_s of a liquid interacting by specified, volume-independent potentials. The first method is based on an application of the approach of Ferrenberg and Swendsen [Phys. Rev. Lett. **61**, 2635 (1988); **63**, 1195 (1989)] to Monte Carlo simulations at two different temperatures; it gives much more reliable results for S_s in liquid Si than previous calculations based on numerical differentiation. The second method expresses the surface entropy directly as a canonical average at fixed temperature.

I. INTRODUCTION

The surface tension τ plays an important role in many properties of liquids. Of equal importance, however, are the various *derivatives* of τ , in particular the temperature derivative $d\tau/dT$ and concentration derivative $\partial\tau/\partial c_i$, where T is the temperature and c_i the concentration of one of the components. These derivatives act as driving forces for convection parallel to the liquid surface whenever the temperature or concentration along the surface is nonuniform. In the low-gravity environment of space, where other gravity-driven sources of convection may be absent, such convection, known as Marangoni convection,¹ may be a dominant process governing fluid motion.

The derivatives of the surface tension are notably difficult quantities to obtain in a computer simulation. The obvious method of direct numerical differentiation of τ is subject to large numerical inaccuracies, particularly since τ itself is usually the result of an extensive numerical calculation. In this paper, we describe two much more accurate methods of computing these derivatives. The first method is an extension of the approach of Ferrenberg and Swendsen,^{2,3} whereby complete thermodynamic information can be obtained over a broad temperature region using only one or a few Monte Carlo simulations. We illustrate the value of this method by using it to compute the surface entropy $S_s \equiv -d\tau/dT$ for a model of liquid Si near the melting temperature, and showing that it gives much more accurate results than direct numerical differentia-

tion. The second method involves expressing the derivatives as explicit canonical averages. This method must give the same results as that of Ferrenberg and Swendsen in the limit of small temperature and concentration differences, but is likely to take somewhat longer to converge.

The remainder of this paper is arranged as follows. In Sec. II and Sec. III, we describe the methods for calculating the surface tension derivatives. A brief discussion follows in Sec. IV.

II. FERRENBURG-SWENDSEN METHOD

We first consider a system of N classical particles interacting by some potential $U(\mathbf{R}_1, \dots, \mathbf{R}_N)$ at temperature T , with some stated boundary conditions. Let $\rho(\{\mathbf{R}_1, \dots, \mathbf{R}_N\}; T)$ denote the probability density that the system of N particles is in a configuration $\{\mathbf{R}_1, \dots, \mathbf{R}_N\}$ at temperature T . The ratio of these two probability densities at different temperatures is

$$\frac{\rho(\{\mathbf{R}_i\}; T_2)}{\rho(\{\mathbf{R}_i\}; T_1)} = \exp \left[H(\{\mathbf{R}_i\}) \left(\frac{1}{k_B T_1} - \frac{1}{k_B T_2} \right) \right]. \quad (1)$$

Thus, if we generate M atomic configurations $\{\mathbf{R}_i\}$ by the usual Metropolis process at temperature T_1 , we can calculate the averages of a thermodynamic quantity A at temperatures T_1 and T_2 from the formulas

$$\langle A(T_1) \rangle = \frac{\sum_{n=1}^M A(\{\mathbf{R}_i\}_n)}{M},$$

$$\langle A(T_2) \rangle = \frac{\sum_{n=1}^M A(\{\mathbf{R}_i\}_n) \exp \left[H(\{\mathbf{R}_i\}_n) \left(\frac{1}{k_B T_2} - \frac{1}{k_B T_1} \right) \right]}{\sum_{n=1}^M \exp \left[H(\{\mathbf{R}_i\}_n) \left(\frac{1}{k_B T_2} - \frac{1}{k_B T_1} \right) \right]}, \quad (2)$$

where $A(\{\mathbf{R}_i\}_n)$ denotes the value of A in the n th configuration at temperature T_1 . By means of these formulas, as first noted by Ferrenberg and Swendsen,^{2,3} we can calculate the average of A at several values of the temperature in a *single* Monte Carlo simulation, with no additional memory and negligible extra computer time. This strategy is very useful in calculating the parameter dependence of various thermodynamic quantities over a limited parameter range. The closer the values of parameters, the more accurate are the results. It is ideally suited to calculating temperature derivatives,

since these require a temperature range which is as small as possible. On the contrary, if these derivatives are calculated through separate runs at different temperatures, the numerical uncertainties will probably overshadow the sought-for differences produced by a very small temperature change.

We apply the Ferrenberg-Swenden (FS) method to obtain the surface entropy $S_s = -d\tau/dT$ of liquid Si. We use the method of Miyazaki, Barker, and Pound⁴ to calculate the surface tension. In this method, the free surface is created in several stages. First, the bulk liquid is simulated through standard Monte Carlo techniques with a cubic supercell of edge a and periodic boundary conditions. Next, the bulk liquid is given two free, parallel surfaces in two steps. In the first step, two of the six faces of the periodic Monte Carlo cell (at $z = -a/2$ and $z = +a/2$) are given hard wall rather than periodic boundary conditions (periodic boundary conditions being maintained in the x and y directions). The free-energy change associated with this change is ΔF_1 . Next, the two hard walls at $z = -a/2$ and $z = +a/2$ are moved adiabatically very far away from the liquid, creating a slab with two free surfaces and periodic boundary conditions in the x and y directions. The change in free energy associated with this process is ΔF_2 . The surface tension is

$$\tau = (\Delta F_1 + \Delta F_2)/2A, \quad (3)$$

where A is the area of one of the free surfaces.

The term ΔF_1 can be written as

$$\Delta F_1 = -k_B T \ln(Q_1/Q_0), \quad (4)$$

where Q_0 and Q_1 are the configurational integrals for the N particles before and after stage 1, i.e.,

$$Q = \int \cdots \int \exp[-U(x_1, \dots, x_N)/k_B T] dx_1 \cdots dx_N, \quad (5)$$

where the indices of Q and U are omitted and U_0 and U_1 are the potential-energy functions before and after stage 1, i.e., with periodic boundary conditions in all three directions, and with hard wall boundary conditions in the z direction. The ratio Q_1/Q_0 can be expressed as the canonical average of an acceptance probability for a Monte Carlo move, using the Metropolis function

$$M(x) = \min[1, e^{-x}]. \quad (6)$$

The result is

$$\frac{Q_1}{Q_0} = \frac{\langle M(U_1^* - U_0^*) \rangle_0}{\langle M(U_0^* - U_1^*) \rangle_1}, \quad (7)$$

where $\langle \rangle_0$ and $\langle \rangle_1$ denote canonical averages taken with potentials U_0^* and U_1^* , and $U_0^* = U_0/k_B T$, $U_1^* = U_1/k_B T$. The Metropolis function can be replaced by other functions, e.g., the Fermi function, which can lead to less numerical uncertainty.⁵

The term ΔF_2 can be similarly calculated as a canonical average. It involves the work required to move the two hard walls to infinity, and can be shown to take the form

$$\Delta F_2 = -k_B T \left(\int_{a/2}^{\infty} \langle n(l) \rangle dl + \int_{-\infty}^{-a/2} \langle n(l) \rangle dl \right), \quad (8)$$

where $\langle n(l) \rangle$ is the atomic number density at the wall, when the wall is at position $z = l$, i.e.,

$$n(l) = \sum_i \delta(l - z_i), \quad (9)$$

z_i being the z coordinate of the i th particle.

We first confirmed that the FS method gives good results for bulk properties, calculating the specific heat C_V for bulk Si using the FS method and from the usual fluctuation expression $C_V = [\langle H^2 \rangle - \langle H \rangle^2]/k_B T^2$ at $T_1 = 1760$ K. In both cases the two- and three-body empirical potentials of Stillinger and Weber⁶ were used. For the purposes of the present calculation, these potentials can be viewed simply as model potentials on which to test two different numerical methods of calculating statistical properties of liquids.⁷ In applying the FS method, we used $T_2 = 1.015T_1$. Both methods gave $C_V = 3.4k_B$ /atom, as quoted in Ref. 7, but the FS method converged in about half as many sweeps through the lattice as the canonical average.

Next, we used the method of FS to calculate the surface entropy $S_s = -d\tau/dT$ for liquid Si at $T = 1760$ K. Table I shows S_s as calculated by direct numerical differentiation and by the method of FS; for comparison, the experimental results of Hardy⁸ are also given. In evaluating the integral for ΔF_2 , we took five steps to move the hard walls to "infinity," i.e., sufficiently far from the liquid as to insure nearly zero liquid density at the wall. The column labeled "FS" is the average of two separate runs, each using a temperature difference of $0.015T$, which yielded $d\tau/dT = -0.189$ and -0.182 dyn/cm K. It is clear that the FS method gives far less numerical uncertainty than the method of numerical differentiation. We also find that about 90% of S_s is due to ΔF_2 , even though this part contributes only about 20% to the surface tension itself. We were unable to draw this conclusion from our previous calculations⁷ because of the much larger uncertainties involved in direct numerical differentiation. As indicated in Ref. 4, the uncertainty of the calculation of ΔF_2 itself is larger than ΔF_1 ; so S_s would be expected to be less precisely known than τ itself. The fact that we obtain results within 4% in two separate runs suggests, however, that this is not a serious problem.

TABLE I. Surface entropy of liquid Si at 1760 K, as calculated using the potentials of Stillinger and Weber, Ref. 6. S_s is the surface entropy, in dyn/cm K. The column labeled FS denotes calculations using the method of Ferrenberg and Swendsen (Refs. 2 and 3), as described in the text. The next column gives results obtained from numerical differentiation in Ref. 7. The uncertainty listed for FS is half the difference between the two separate Monte Carlo simulations from which these results were obtained, while that given for Ref. 7 is a judgment about numerical uncertainties involved in calculating differences between Monte Carlo data at two different temperatures. Experimental results are due to Hardy (Ref. 8).

	FS	Ref. 7	Expt.
$-S_s(d\tau/dT)$	$-0.186(\pm 0.004)$	$-0.2(\pm 0.2)$	$-0.28, -0.13$

III. SURFACE ENTROPY AS A CANONICAL AVERAGE

Next, we describe a method to compute $S_s = -d\tau/dT$ directly as an average in the canonical ensemble. Given this expression, the derivative can be obtained, in principle, to the same accuracy as the surface tension itself, working only at a single temperature. This approach is an alternative to the FS method, and is operationally distinct from it, although it must, of course, yield the same derivative. By analogy with our findings in the calculation of specific heat, we expect that the FS method will converge more rapidly. Nevertheless, it is useful to have an explicit expression for the surface entropy, which can be evaluated by standard Monte Carlo techniques.

We begin by writing down the well-known expression for the average of any quantity $A(T)$ in the classical canonical ensemble at temperature T . Denoting the canonical average by $\langle \rangle$, we have

$$\frac{d\langle A \rangle}{dT} = \left\langle \frac{dA}{dT} \right\rangle + \frac{1}{k_B T^2} [\langle AH \rangle - \langle A \rangle \langle H \rangle], \quad (10)$$

where H is the Hamiltonian. Now the surface tension, from Eq. (3), is the sum of two terms involving free-energy changes ΔF_1 and ΔF_2 . From Eqs. (4)–(7), we obtain

$$\frac{d\Delta F_1}{dT} = \frac{\Delta F_1}{T} - k_B T G, \quad (11)$$

where

$$G = \frac{(d/dT)\langle M(U_1^* - U_0^*) \rangle_0}{\langle M(U_1^* - U_0^*) \rangle_0} - \frac{(d/dT)\langle M(U_0^* - U_1^*) \rangle_1}{\langle M(U_0^* - U_1^*) \rangle_1}. \quad (12)$$

The temperature derivatives in this equation can readily be calculated, using Eq. (6), to give

$$\frac{d}{dT}\langle M(U_1^* - U_0^*) \rangle_0 = \frac{1}{k_B T^2} [2\langle MU_0 \rangle_0 - \langle MU_1 \rangle_0 - \langle M \rangle_0 \langle U \rangle_0], \quad (13)$$

$$\frac{d}{dT}\langle M(U_0^* - U_1^*) \rangle_1 = \frac{1}{k_B T^2} [2\langle M'U_1 \rangle_1 - \langle M'U_0 \rangle_1 - \langle M' \rangle_1 \langle U_1 \rangle_1], \quad (14)$$

where we have used the notation

$$M \equiv M(U_1^* - U_0^*), \quad (15)$$

$$M' \equiv M(U_0^* - U_1^*). \quad (16)$$

Likewise, the second term in the surface entropy takes the form

$$\frac{d\Delta F_2}{dT} = \frac{\Delta F_2}{T} - k_B T \left[\int_{a/2}^{\infty} \frac{d\langle n(l) \rangle}{dT} dl + \int_{-\infty}^{-a/2} \frac{d\langle n(l) \rangle}{dT} dl \right], \quad (17)$$

where

$$\frac{d\langle n(l) \rangle}{dT} = \frac{1}{k_B T^2} [\langle n(l)U_1 \rangle - \langle n(l) \rangle \langle U_1 \rangle]. \quad (18)$$

U_1 and $n(l)$ are defined below Eq. (5) and in Eq. (9), and the averages are to be calculated with the walls at $\pm l$. Using these formulas, the surface entropy can be calculated by explicit integrals and canonical averages, to the same accuracy as the surface tension itself. Like the surface tension, S_s must be evaluated by a two-step process as in Refs. 4 and 5.

IV. DISCUSSION

We have presented two practical methods for direct computation of the surface entropy of a liquid without the necessity of explicit numerical differentiation of the surface tension. The first, based on the technique of Ferrenberg and Swendsen, is shown to give much more reliable numerical values of this quantity than numerical differentiation. The second method, although not tested numerically here, should give similarly reliable results and hence be useful in many applications.

Similar expressions can readily be derived for concentration derivatives of the surface tension. This derivative, which is equally important in studies of convection at liquid surfaces, is even more difficult than the surface entropy to compute from numerical differentiation. We plan to present such calculations in a subsequent publication.

ACKNOWLEDGMENTS

We are grateful for many useful conversations with A. J. Markworth. This work was supported by the U.S. National Aeronautics and Space Administration through Grant No. NAG3-999 and by the Ohio Supercomputer Center through a grant of time on the Cray Y-MP8/864.

¹For a discussion, see, e.g., Y. Kamotani, S. Ostrach, and S. Lowry, in *Materials Processing in the Reduced Gravity Environment of Space*, edited by G. Rindone (North-Holland, Amsterdam, 1982), pp. 161–172; or T. J. McNeil, R. Cole, and R. S. Subramanian, *ibid.* pp. 289–300.
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