Surface tension, hydrophobicity, and black holes: The entropic connection

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The geometric entropy arising from partitioning space in a fluid "field theory" is shown to be linearly proportional to the area of an excluded region. The coefficient of proportionality is related to surface tension by a thermodynamic argument. Good agreement with experimental data is obtained for a number of fluids. The calculation employs a density-matrix formalism developed previously for studying the origin of black hole entropy. This approach may lead to a practical technique for the evaluation of thermodynamic quantities with important entropic components. [S1063-651X(96)11304-0]

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I. PROLEGOMENA

The ground state of a quantum field theory can be described by means of a density matrix. If the field degrees of freedom inside a specified volume are traced over, the result is a reduced density matrix ρ_{out} which depends only on the degrees of freedom external to the excluded volume. Associated with this reduced system is a geometric entropy, $S_{\text{out}}/k = -\text{Tr}(\rho_{\text{out}} \ln \rho_{\text{out}})$, which quantifies the information lost by the partitioning of space. The geometric entropy is an expression of the fact that ρ_{out} lacks the information contained in correlations between the excluded interior volume and the rest of the system.

This density-matrix formalism was recently utilized in an attempt to provide a simple explanation for the classic result [1] that the entropy of a black hole is linearly proportional to its surface area. A spherical volume of a space containing a free scalar field was excluded, and the resultant geometric entropy was then determined. It was found [2,3] that the geometric entropy of this black hole is, in fact, proportional to the area of the excluded region, rather than to its volume. This result seems initially to be rather mysterious, since entropy (like free energy) is generally an extensive quantity. However, in several important physical situations, major contributions to the free energy of a system are, in fact, proportional to its area. These area law contributions are primarily responsible for liquid surface tension and for hydrophobic effects central to protein folding.

Although the density-matrix formalism was developed to further our understanding of black holes, it does not directly utilize either classical general relativity or quantum gravity. It will be shown here that geometric entropy can be used to exhibit a point of commonality between liquid surface tension and the aforementioned results, which are germane to the study of black holes. The geometric entropy arising from partitioning space in an empirical fluid field theory is calculated. Remarkably, the geometric entropy is found to be linearly proportional to the area of the excluded volume, as in the above case [2,3] of a free scalar field. A thermodynamic argument relates the coefficient of proportionality to liquid surface tension. Good agreement with experiment is obtained for a number of liquids, suggesting that the density-matrix formalism may lead to a simple and accurate way to evaluate thermodynamic quantities with important entropic components. Further anticipated developments are mentioned in the closing remarks.

II. FIELD THEORY OF FLUIDS

The applicability of the density-matrix formalism to fluids is founded upon the observation that a liquid at finite temperature can be considered, for some purposes, as the vacuum state of a field theory. This is a natural step to take, since the structure and properties of a fluid at equilibrium can be described by its molecular distributions [4,5]. These distributions can, in turn, be used to define the Green's functions of a field theory, e.g.,

$$\langle \rho(\mathbf{r}') \rangle = \rho_0 ,$$

$$\langle \rho(\mathbf{r}') \rho(\mathbf{r}'+\mathbf{r}) \rangle = \rho_0^2 [1 + h(\mathbf{r})] + \rho_0 \delta(\mathbf{r}), \qquad (1)$$

where the right-hand sides of Eqs. (1) are independent of $\mathbf{r}'$ for a homogeneous fluid.

These Green's functions $\langle\rangle$ are vacuum (i.e., ground state) expectation values of fluid density fields $\{\rho(\mathbf{r})\}$, calculated by means of a functional integral measure defined below. The complete set of Green's functions, which can be taken as the definition of a field theory, can likewise be expressed in terms of higher-order molecular distributions. The average fluid number density ρ_0 and pair correlation function $h(\mathbf{r})$ are physically measurable, and can be extracted from experimental data. The first two Green's functions are thus known quantities.

The idea of representing a fluid at finite temperature by the vacuum state of a field theory is quite unusual, and therefore deserves careful explanation. Relations such as Eqs. (1) are frequently found in the classical treatments of fluids [4,5]. However, in the classical treatment the averages $\langle\rangle$ are meant to be taken over canonical or grand canonical ensembles. Thus, although the definitions Eqs. (1) are identical to equations commonly found in textbooks, their interpretation is quite different.

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In the classical formalism, one usually begins by taking averages over a canonical ensemble of N particles which interact via a potential function $V(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$. Then the canonical ensemble averages $\langle\rangle_{\text{canonical}}$ of densities and their correlations are defined by relations like

$$\langle\rho(\mathbf{r})\rangle_{\text{canonical}}=Z_N^{-1}\int d\mathbf{r}_1\int d\mathbf{r}_2\cdots \times\int d\mathbf{r}_N\exp(-\beta V)\rho_{\text{classical}}(\mathbf{r}),$$

where

$$\rho_{\text{classical}}(\mathbf{r})\equiv\sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{r}_i).$$

The integration is over the coordinates of all particles 1 through N, $\beta\equiv 1/kT$ is the inverse temperature, and Z_N is the partition function. Grand-canonical averages can then be calculated in the usual fashion to yield the familiar molecular distributions.

One can thus generate an infinite set of grand-canonical expectation values

$$\langle\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)\cdots\rho(\mathbf{r}_M)\rangle_{\text{gc}}$$

for all products of the quantity $\rho_{\text{classical}}(\mathbf{r})$. It is then that an unusual step is taken. Each grand-canonical average $\langle\rangle_{\text{gc}}$ is identified with the corresponding Green's function of a certain field theory. Because the complete set of grand-canonical expectation values is known in principle, all of the Green's functions of this field theory are also known. The full set of Green's functions for a field theory can then be taken as a definition of that field theory. One important point must be emphasized, however: field-theoretic Green's functions are, *by definition*, expectation values of certain operators taken over the vacuum state. Thus, if the operators and field-theoretic ground state are chosen so as to reproduce the hierarchy of grand-canonical expectation values discussed above, the ground state of a field theory provides a description of a fluid that is *precisely equivalent* to knowledge of the complete set of molecular distributions.

In practice, of course, neither field theories nor grand-canonical fluid models are generally solvable. Thus one must resort to judicious approximation. As the present study is primarily intended to illustrate the potential benefits of a different approach, the field theory used is a simple one: a generalized free field theory chosen to reproduce only the first two Green's functions Eqs. (1).

The simplest field theory whose Green's functions reproduce Eqs. (1) has a ground-state density matrix proportional to $\exp[-1/2(S\{\rho\}+S\{\rho'\})]$, where S is quadratic in the field variables $\{\rho(\mathbf{r})\}$:

$$\rho_s S\{\rho\}=\tfrac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'[\rho(\mathbf{r})-\rho_0]W(\mathbf{r}-\mathbf{r}')[\rho(\mathbf{r}')-\rho_0],$$
$$W(\mathbf{r}-\mathbf{r}')\equiv\delta(\mathbf{r}-\mathbf{r}')-\rho_0 c(\mathbf{r}-\mathbf{r}') \tag{2}$$

and the function $c(\mathbf{r}-\mathbf{r}')$ remains to be determined. As an additional convenience, the field variables $\{\rho(\mathbf{r})\}$ are allowed to range from negative to positive infinity. The expectation values in Eqs. (1) are calculated via the functional integral

$$\langle O\rangle\equiv\Xi^{-1}\int O\{\rho\}\exp[-S\{\rho\}]D\rho,$$
$$\Xi\equiv\int\exp[-S\{\rho\}]D\rho. \tag{3}$$

The function $c(\mathbf{r})$ is then required via Eq. (1) to satisfy

$$h(\mathbf{r})=c(\mathbf{r})+\rho_0\int c(\mathbf{r}-\mathbf{r}')h(\mathbf{r}')d\mathbf{r}', \tag{4}$$

which is the well-known Ornstein-Zernike relation [6] linking the direct correlation function $c(\mathbf{r})$ with the pair correlation $h(\mathbf{r})$. The physical meaning of the function $c(\mathbf{r})$ is thus manifest. The success of the Ornstein-Zernike approach derives in part from the short-ranged character of $c(\mathbf{r})$, suggesting that Eq. (2) is, indeed, a sensible starting point.

For this choice of $c(\mathbf{r})$, Eqs. (2) and (3) reproduce Eqs. (1). The constraints posed by Eqs. (1) alone are, however, insufficient to define a field theory uniquely. The generalized free field theory implicit in Eqs. (2) and (3) is only the simplest solution of Eqs. (1), and therefore provides an approximate description of a real liquid. In the theory defined here, all higher-order correlations are calculable in terms of products of those in Eqs. (1). The fluid theory defined by Eqs. (2) possesses the property that higher-order molecular distributions factorize, which is known [5] to be correct for large separations. There is no barrier of principle to performing a more elaborate calculation with a better model of a fluid; however, the labor of calculation would be larger. (This point is discussed in further detail below.) The integration over unphysical negative values of the fluid density fields $\{\rho(\mathbf{r})\}$ is also permissible, for $S\{\rho\}$ is positive definite and is sharply peaked about $\rho(\mathbf{r})\cong\rho_0>0$, provided that the Fourier transform $\tilde{W}(k)$ is positive (as it is for a fluid with finite compressibility). Although negative, virtual values of the density appear formally in the functional measure Eq. (3), negative densities do not explicitly enter into the physically observable molecular distributions, which are the Green's functions of the theory. The standard [5] density functional approach can be recovered by adding the usual potential term $\int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$ to $S\{\rho\}$, and then evaluating Ξ as a functional of the average densities $\bar{\rho}(\mathbf{r})\equiv\langle\rho(\mathbf{r})\rangle_v$. The density functional $\Omega\{\bar{\rho}\}$ of the bulk fluid is then simply $\Omega\{\rho_0\}-kT\ln[\Xi\{\bar{\rho}\}]$, which is the effective action of the field theory Eq. (3). For any $S\{\rho\}$, $\Omega\{\bar{\rho}\}$ calculated in this fashion is convex [7] for a uniform system, and can have no more than one minimum, so no Maxwell construction is needed.

In what follows, the fluid density ρ_0 and pair correlation function $h(\mathbf{r})$ are taken from experimental results. No attempt is made to derive either of these quantities from first principles. One final simplification is therefore employed in the sequel. Experimental techniques (such as x-ray scattering) typically measure only a spherical average $h(|\mathbf{r}|)$ of the pair correlation. Although the above formalism can be easily applied to test a nonspherically symmetric *model*, using real

data requires the assumption that $h(\mathbf{r})=h(|\mathbf{r}|)$ and $c(\mathbf{r})=c(|\mathbf{r}|)$. This assumption is, however, commonplace [12].

III. RELATING GEOMETRIC ENTROPY TO SURFACE TENSION

The geometric entropy can be related to fluid surface tension by a simple argument. A well-known result of statistical mechanics [8] states that the probability of observing a fluctuation in a system at temperature T is given by $\exp(-W/kT)$, where W is the reversible work required to produce the fluctuated configuration through the application of a constraint, and k is Boltzmann's constant. Thus the reversible work required to produce a cavity of low density in a fluid can be found from the probability that such a cavity occurs via a fluctuation. Consider a subsystem of the fluid contained within an imaginary sphere of radius R. The density matrix ρ_{in} for this subsystem can be constructed from that given above for the full volume by integrating out the field variables $\{\rho(\mathbf{r})\}$ outside the sphere. This density matrix is a weighted sum of the states internal to the sphere, given that the exterior region is unobserved. It is shown below that, ignoring volume work, the relative probability of the occurrence of any state which approximates a low-density cavity is essentially $\exp(-S_{\text{in}}/k)$, where $S_{\text{in}}/k=-\text{Tr}(\rho_{\text{in}}\ln\rho_{\text{in}})$ is equal to the geometric entropy S_{out}/k of the subsystem. The macroscopic surface tension γ for a fluid at a fixed temperature T is then the large R limit of $TS_{\text{in}}(4\pi R^2)^{-1}$. Since the Green's functions used to specify the fluid field theory depend implicitly upon the liquid temperature, geometric entropy surface tension varies nonlinearly with temperature, and thus contains contributions from both surface excess entropy and enthalpy.

The useful correspondence between this surface tension calculation and the aforementioned black hole entropy result arises upon construction of the complementary density matrix ρ_{out}. In this complementary case, only the fields $\{\rho(\mathbf{r})\}$ *inside* the sphere are integrated out to yield ρ_{out}. Then it can be shown [3] that $S_{\text{in}}/k=S_{\text{out}}/k=-\text{Tr}(\rho_{\text{out}}\ln\rho_{\text{out}})$, where S_{out}/k is the geometric entropy of the subsystem. The density-matrix calculations [2,3] relevant to black hole entropy involve the development of techniques for calculating S_{out}; by the reasoning given here, they are also useful for extracting liquid surface tension.

The density-matrix calculation proceeds as follows. When the field variables $\{\rho(\mathbf{r})\}$ outside the sphere are integrated out, the result [2] is a reduced density matrix

$$\rho_{\text{in}}\{q,q'\}=[\det(M/\pi)]^{1/2}\exp[-\tfrac{1}{2}(qMq+q'Mq')-\tfrac{1}{4}(q-q')N(q-q')], \tag{5}$$

where $\{q(\mathbf{r})\equiv[\rho(\mathbf{r})-\rho_0]\}$ inside the sphere. The matrix M is the inverse of $W/(2\rho_0)$, taken over this interior domain, while $N\equiv W/(2\rho_0)-M$. Since this domain is finite, M and N are to be considered sums over discrete values of wave number.

The reduced density matrix ρ_{in} is next expressed in a basis $\{x\}$ in which the matrix $\Lambda_S\equiv M^{-1/2}NM^{-1/2}$ is diagonal, with eigenvalues λ. The coordinates $\{x\}$ are normalized by $x^2=qMq$, so that the determinant prefactor in Eq. (5) is eliminated. Then [2,3] for each mode [with eigenvalue $\lambda\equiv 4\xi(1-\xi)^{-2}$, $0\leq\xi\leq 1$]:

$$\rho_{\text{in},\lambda}\{x,x'\}=\sum_{n=0}^{\infty}p_n\Psi_n(x)\Psi_n(x'), \tag{6}$$

$$\Psi_n(x)\equiv(2^n n!\times\sqrt{\pi/\alpha})^{-1/2}H_n(\sqrt{\alpha}x)\exp(-\alpha x^2/2), \tag{7}$$

where $H_n(z)$ is a Hermite polynomial, $\alpha\equiv(1+\xi)/(1-\xi)$, and $p_n=(1-\xi)\xi^n$. The reduced density matrix is a product of those for each mode λ:

$$\rho_{\text{in}}\{x,x'\}=\prod_{\lambda}\rho_{\text{in},\lambda}\{x,x'\}. \tag{8}$$

Each mode $\rho_{\text{in},\lambda}$ behaves like a thermal density matrix for a harmonic oscillator, specified by a frequency α and effective temperature $T_{\text{eff}}=\alpha/\ln(1/\xi)$.

The probability that a mode λ of the spherical subsystem is found in state n is thus p_n. Associated with this probability distribution are two useful quantities. These are $\bar{n}$, which is the average state number,

$$\bar{n}=\sum_{n=0}^{\infty}np_n=\xi/(1-\xi), \tag{9}$$

and S_{in}, the geometric entropy, in terms of which the density of states is $\exp(-S_{\text{in}}/k)$:

$$S_{\text{in}}/k=-\sum_{n=0}^{\infty}p_n\ln p_n=-\ln(1-\xi)-\bar{n}\ln\xi. \tag{10}$$

The probability of finding the mode in any state $n\geq N$ is $p_{\text{any}}(N)=\xi^N$. Thus, for $n\geq\bar{n}$,

$$p_n\leq p_{\bar{n}}=\exp(-S_{\text{in}}/k)\leq p_{\text{any}}(\bar{n}). \tag{11}$$

For the systems of interest here, ξ is generally quite small, so the second inequality is nearly an equality:

$$\exp(-S_{\text{in}}/k)\cong p_{\text{any}}(\bar{n}). \tag{12}$$

In the classical methods of calculation, the probability that the system attains a given density is calculated. The course taken here is, however, conceptually quite different. The quantity of interest here is the relative probability to find the subsystem in certain *states*, those whose characteristic density is relatively low. For a given state, there is a finite probability that any value of the density will be attained. The expectation value of an operator can, however, be determined for such a state. Thus the expectation value of $x^2\sim(\Omega\{\rho\}-\Omega\{\rho_0\})/kT$ in state n is given by $(n+\frac{1}{2})/\alpha$. The probability distribution $[\Psi_n(x)]^2$ for $n>0$ typically is maximized when $x\cong x_{\text{peak}}\equiv\pm[(2n+1)/\alpha]^{1/2}$, corresponding to values of the density that are above and below the bulk value. A state whose density is expected to differ from the bulk value by at least the inverse volume of the subsystem (so that at least one molecule is absent) must therefore have $n\geq\bar{n}$. By Eq. (12), the probability of finding the system in such a state is well approximated by $\exp(-S_{\text{in}}/k)$.

Where, then, are the approximations made, and how does one deal with more complex situations? Let us review the logic of the calculation. One begins with a field theory in its ground state. The question of interest is the probability that a given fluctuation occurs inside an imaginary sphere of radius R, regardless of what occurs outside that imaginary sphere. Thus the degrees of freedom outside the imaginary sphere are integrated out. What remains is a field theory that is defined in terms of variables internal to the sphere. This field theory gives the relative probability of a given internal configuration, assuming that the region external to the sphere is unobserved. In this regard, there is a point of contrast between the fluid calculation and the black hole entropy result. In the latter case, degrees of freedom inside the black hole are considered *unobservable* on fundamental grounds, rather than simply being *unobserved*. Nevertheless, the correct formal procedure is the same in the two cases—the unobserved variables are integrated out.

It is important to realize that, at least in principle, no approximations need to be made to reach this stage of the calculation. Instead of the quadratic form given in Eq. (2), one could just as well begin with an arbitrarily complex density functional $S\{\rho\}$, corresponding to an arbitrary set of molecular distributions. The virtue of the simple form Eq. (2) is that it allows the calculation of the reduced density matrix to be made explicit. Nevertheless, by perturbative or numerical means, it is presumably possible to evaluate the density matrix for the system inside the imaginary sphere for an arbitrary density functional $S\{\rho\}$. The result for each eigenmode of the density matrix will be formally identical to Eq. (6), although the eigenfunctions Ψ_n will no longer be the explicit forms of Eq. (7). Thus the simple generalized free-field theory implied by Eq. (2) is a calculational convenience, rather than an integral part of the formalism. Moreover, as is seen below, this simple functional form suffices to reproduce not only the necessary area-law form of the geometric entropy (implying a constant surface tension), but gives reasonable answers for the surface tension as well.

The next step in the analysis is the calculation of the probability to find the interior region in states whose expected density is less than the bulk value. Another point must be made clear here. Although the surrounding imaginary sphere represents a sharp boundary, the interface itself is not constrained to be as sharp. It is only necessary that the boundary of the imaginary sphere be placed outside the interface region. Thus one could imagine making the imaginary sphere extremely large, and asking the probability to observe states of density only slightly less than the bulk value. For a sufficiently large sphere and small deviation from bulk density, the quadratic approximation to the density functional $S\{\rho\}$ must therefore be valid. For a small sphere, however, there will be an error in estimating the size of the bubble of low density contained within the sphere. The size of the interface region should be dictated by molecular dimensions. (In other words, the existence of an interface in a noncritical system should not perturb the system strongly more than a few molecular diameters away from that interface.) Thus the ratio of the interface width to the sphere size should vanish for a large enough sphere (which is, of course, the limit of interest for macroscopic surface tension). Therefore, for a large enough sphere, the area of the low-density bubble is asymptotically equal to the area of the surrounding imaginary sphere.

If a different problem is formulated, such as the calculation of the boundary free energy associated with a bulk liquid in contact with a hard wall, constraints on the selected configurations must be introduced. For the boundary free energy problem, the density must be zero at the wall. Thus, rather than asking [as in Eq. (12)] the probability $p_{\rm any}(N)$ to find a mode in any state greater than N, one asks the probability to find states with a node in the proper location. A more detailed analysis would be needed in order to select the proper states to include in this sum. However, in any case, there must be factors of p_n included in the calculation, and thus there should also always be a connection to the geometric entropy. This relation should persist even if a better model of a fluid than Eq. (2) is used.

At least for some problems, it is possible to improve upon the results given by the approximate quadratic density functional $S\{\rho\}$ by means of a simple perturbative analysis, although in general such improvements likely require numerical simulation. One example of how a perturbative study might proceed is as follows. Consider a more elaborate model of a fluid constructed by replacing the probability functional $\exp[-S\{\rho\}]$ defined by Eq. (2) with a functional

$$\exp[-S_{\rm new}\{\rho\}]=\exp[-S\{\rho\}]+\epsilon\,\exp[-S_{\rm gas}\{\rho\}],$$

where $\rho_0 S_{\rm gas}\{\rho\}=1/2\int[\rho(\mathbf{r})]^2 d\mathbf{r}$. Here ϵ is a small number that gives the relative probability of the bulk fluid to be in the gas phase. The action $S_{\rm new}\{\rho\}$ has two minima, essentially at zero density $\rho=0$ and at the bulk density $\rho=\rho_0$, and thus includes a crude characterization of the gas phase of the fluid. One can then calculate, using ordinary quantum-mechanical perturbation theory, the change in the eigenvalues ρ_n of the density matrix $\rho_{\rm in}$ due to the additional term in $\exp[-S\{\rho\}]$. The gas-phase contributions to the geometric entropy $-\Sigma\rho_n\ln\rho_n$ can then be expanded in a series in the small number ϵ, allowing geometric entropy to be determined in a controlled fashion.

It is therefore clear that no barrier of principle exists in applying the techniques developed here to fluid models of arbitrary complexity. The present formalism is thus not subject to the easy criticism [9] applied to early integral-equation treatments of surface tension. In these early calculations, the direct correlation function appropriate to a bulk fluid was employed essentially to estimate the relative probability of various interfacial configurations, whose local density was necessarily far from its bulk value. These calculations were thus highly sensitive to the tails of the probability distribution employed, while the bulk direct correlation only provides information about the distribution near its peak. The present argument obviates this difficulty by counting states, since the specific form of the density matrix for densities far from the bulk value contributes little to $S_{\rm in}/k=-{\rm Tr}(\rho_{\rm in}\ln\rho_{\rm in})$. Thus, by calculating the geometric entropy, one is determining the relative probability of the system to be in a state whose typical density is *outside* the region where the probability distribution is maximized. Since both the distribution near its peak and the overall normalization of the probability distribution are known, this calcula-

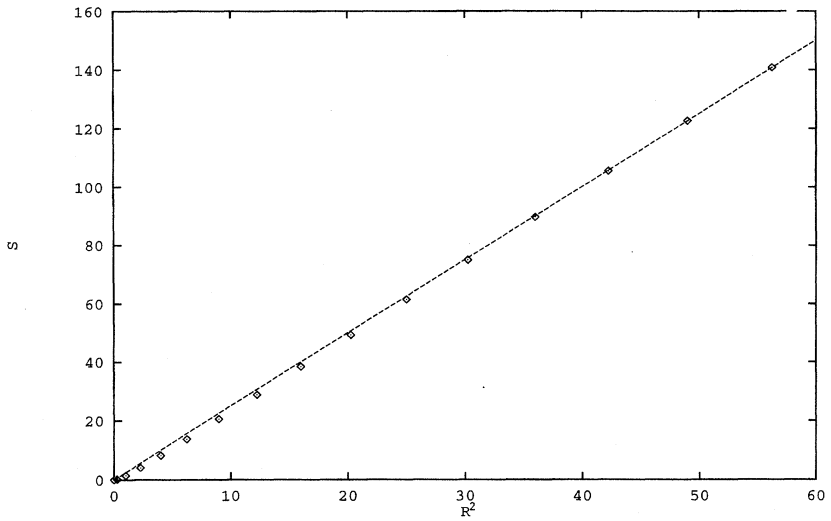

FIG. 1. Plot of $S_{\rm out}(R)$ vs R^2 (Å^2) for water. The dashed line is the function $2.50R^2$, displayed for comparison with plotted data points.

tion can be done relatively accurately. Moreover, as the density matrix $\rho_{\rm in}$ is constructed by integrating over all fields $\{\rho(\mathbf{r})\}$ external to the sphere, correlations of arbitrarily long wavelength are included, as they should be [5,9]. Nevertheless, as discussed above, if the effects of complex boundary conditions are to be accounted for in a satisfactory way, further constraints on the available states must be included.

IV. EVALUATION OF SURFACE TENSION

The calculation of $S_{\rm out}$ is easily performed using Eq. (34) of Ref. [2]. The asymmetric matrix $\Lambda \equiv M^{-1}N$ has the same eigenvalues as the symmetric matrix $\Lambda_S \equiv M^{-1/2}NM^{-1/2}$, but is easier to construct numerically. Therefore, the eigenvalues of Λ are computed. By making an expansion in spherical harmonics, the problem reduces to finding the eigenvalues λ_l of the matrix

$$\Lambda_l(r,r'') = -\int_0^R T_l[1/\tilde{W}](r,r')T_l[\tilde{W}](r',r'')r'^2dr', \tag{13}$$

with respect to the measure $(r'')^2dr''$ over the interval $\{r,r''>R\}$, where

$$T_l[\tilde{W}](r',r'') \equiv (r'r'')^{-1/2}\int_0^\infty kdk\ \tilde{W}(k)J_{l+(1/2)}(kr') \times J_{l+(1/2)}(kr''), \tag{14}$$

and similarly for $T_l[1/\tilde{W}]$. Here $\tilde{W}(k)$ is the Fourier transform of $W(r)$, while $J_{l+(1/2)}(z)$ is a Bessel function. Then [2]

$$S_{\rm out}/k = \sum_{l=0}^{\infty}(2l+1)\{\ln(\tfrac{1}{2}\lambda_l^{1/2}) + (1+\lambda_l)^{1/2}\ln[(1+\lambda_l^{-1})^{1/2}+\lambda_l^{-1/2}]\}. \tag{15}$$

The sum in Eq. (15) is taken over all eigenvalues λ_l for each l. The function $\rho_0\tilde{h}(k) = 1/\tilde{W}(k) - 1$ is taken directly from experiment, obviating the need for an independent determination of the density ρ_0. As k increases, $\tilde{h}(k)$ goes to zero. Hence the substitutions

$$1/\tilde{W}(k) \to \rho_0\tilde{h}(k) \equiv \tilde{w}^{-1}(k), \tag{16}$$

$$\tilde{W}(k) \to -\rho_0\tilde{h}(k)/[1+\rho_0\tilde{h}(k)] \equiv \tilde{w}(k) \tag{17}$$

were made in Eqs. (13) and (14) to ensure the convergence of the integrals Eq. (14). Since $T_l[1](r,r') = (r)^{-2}\delta(r-r')$, subtracting one from $\tilde{W}(k)$ [or $1/\tilde{W}(k)$] leaves $\Lambda_l(r,r'')$ unaffected for $\{r,r''>R\}$, and so the sum Eq. (15) is unchanged by this replacement. In contrast to the case [2,3] of a massless scalar field theory [where $\tilde{W}(k)=k$], no ultraviolet cutoff is needed here, since $\tilde{h}(k)$ vanishes for large k. Data are generally presented as a set of N values of $\rho_0\tilde{h}(k)$ at uniformly spaced intervals of $k=n(\Delta k)$, so the integrals Eq. (14) can be viewed as finite trapezoid-rule sums. The eigenvectors of $\Lambda_l(r,r'')$ are linear combinations of

$$u_l(k,r'') = \Theta(r''-R)(r'')^{-1/2}J_{l+(1/2)}(kr'') \tag{18}$$

for values of k contained within the data set, reducing the problem to a numerical diagonalization of the $N\times N$ matrix

$$\Lambda_l(m,n) = -m[\tilde{w}^{-1}(m\Delta k)]\sum_{i=1}^{N} I_l(m,i)[\tilde{w}(i\Delta k)] \times [\delta_{\rm in} - iI_l(i,n)] \tag{19}$$

for each l. The required indefinite integrals of Bessel functions

$$I_l(m,n) \equiv \int_0^{R\Delta k} J_{l+(1/2)}(ms)J_{l+(1/2)}(ns)s\ ds \tag{20}$$

can be performed analytically. The computational procedure was checked against the test case $h(r) = -\exp(-mr)$, for which the integrals Eq. (14) are known exactly.

TABLE I. Surface tension γ (dyn/cm).

	DM	Experiment	SPT
Sodium	164 (373 K)	206 (371 K)	91 (371 K)
Potassium	93 (338 K)	88 (337 K)	56 (337 K)
Water	82 (298 K)	72 (298 K)	52 (303 K)
Chlorine	31 (298 K)	18 (293 K)	20 (293 K)
Methane	21 (96 K)	16 (95 K)	
Nitrogen	6.4 (77 K)	9 (77 K)	9 (77 K)

The geometric entropy $S_{\text{out}}(R)$ for water at 25 °C was calculated by applying the above procedure to structure function data [10]. The summand of Eq. (15) vanishes exponentially with l, albeit with a large decay length (~ 10). By including all values of $l \leq 75$, $S_{\text{out}}(R)$ can be accurately calculated up to $R \sim 7.5$ Å. Figure 1 displays the result. Except for very small R values, $S_{\text{out}}(R)$ is linearly proportional to R^2, as it is for a cutoff scalar field theory [2,3]. Asymptotically, $S_{\text{out}}(R) \sim 2.50R^2$, yielding a surface tension of 82 dyn/cm, which is 14% larger than the experimental number 72 dyn/cm [11]. For comparison, scaled particle theory using the usual hard-sphere radius of 2.7 Å predicts [13] 52 dyn/cm at 303 K. A detailed molecular dynamics simulation [14] of water at 305 K yields 67 dyn/cm, to be compared with the 71 dyn/cm obtained experimentally at this temperature. These simulation results can be *fitted* by scaled particle theory, if the significantly larger value of 2.875 Å is chosen for the hard-sphere radius of water. [As there are several implicit scales present, dimensional analysis cannot be used to obviate the density-matrix entropy calculation. Scaled particle theory, where surface tension is given in terms of the hard-sphere radius a by the form $\gamma = kT/a^2 f(\rho_0 a^3)$, is probably the simplest viable alternative. Indeed, the only external input to the density-matrix calculation, $\rho_0 \tilde{h}(k)$, is dimensionless.]

The surface tension of a number of other liquids was also calculated using their measured structure functions [15,16]. The density-matrix (DM) results are given in Table I, along with experimental data [11,13,17] and available estimates [13] from scaled particle theory (SPT). The agreement between the density-matrix results and experimental data over a wide temperature range is respectable, especially since the only input to the calculation is the (measured) structure factor. By contrast, scaled particle theory is quite sensitive to the value chosen for the hard-sphere radius. This parameter is not measurable directly, and is usually determined by fitting compressibility data. The closest agreement between experiment and the density-matrix calculation occurs for sodium, potassium, and water, whose structure functions are known with the best precision.

V. CONCLUSIONS

It is worth emphasizing the remarkable fact that the geometric entropy was found to be essentially a linear function of the area in every case considered here, in addition to the free scalar field theory considered previously by others [2,3]. On very general grounds [3], the eigenvalues of the reduced density matrix (and thus the geometric entropy) depend upon the area of the boundary surface, and not upon the volume of the excluded region. However, it is not clear why the geometric entropy should be linearly proportional to this area, especially for situations whose physical basis and mathematical structure are substantially different. (Thus, for example, the calculation of geometric entropy in the black hole case required the introduction of an ultraviolet cutoff; here, since the structure factor of a fluid vanishes at large wave number, no cutoff is needed.) Moreover, the linear dependence of geometric entropy on area provides an additional point of support for the present mode of calculation. It not only gives the correct area-law form for this contribution to the free energy, but gives reasonable values for the constant of proportionality (which is the surface tension).

As a rule, few ideas relevant to quantum gravity have practical applications. One exception was given here. By determining the geometric entropy of a black hole in a fluid field theory, the liquid surface tension can be evaluated in an interesting way. These calculations are essentially exact results for a field theory that is an approximation to a real liquid. The procedure is therefore automatically self-consistent, which may partly account for its plausible accuracy. Possible extensions of the formalism include an extraction of the hydrophobic potential of mean force, which is a major ingredient of protein folding models [18]. This may be determined by excluding two regions of fluid and calculating the resultant geometric entropy as a function of the distance between them. The density-matrix method is sensitive to the form of the structure factor over its entire range. Thus the method may provide a useful test of approximate theories. The major virtue of the density-matrix method is its relative simplicity—molecular simulations of entropic quantities are difficult and, hence, rare. Further calculations are in progress.

Note added in proof. Recently, we have become aware of work [19] in which mathematically similar ideas are explored.

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[1] J. D. Bekenstein, Phys. Rev. D **7**, 2333 (1973); **9**, 3292 (1974); S. W. Hawking, Commun. Math. Phys. **43**, 199 (1975); G. W. Gibbons and S. W. Hawking, Phys. Rev. D **15**, 2752 (1977).

[2] L. Bombelli, R. K. Koul, J. Lee, and R. D. Sorkin, Phys. Rev. D **34**, 373 (1986).

[3] M. Srednicki, Phys. Rev. Lett. **71**, 666 (1993). See also C. Callan and F. Wilczek, Phys. Lett. B **333**, 55 (1994); V. P. Frolov, Phys. Rev. Lett. **74**, 3319 (1995).

[4] J. S. Rowlinson and F. L. Swinton, *Liquids and Liquid Mixtures* (Butterworth Scientific, London, 1982); J. P. Hansen and

I. R. McDonald, *Theory of Simple Liquids* (Academic, New York, 1976).
[5] J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Clarendon, Oxford, 1982). See also R. Evans, Adv. Phys. **28**, 143 (1979).
[6] L. S. Ornstein and F. Zernike, Proc. Akad. Sci. (Amsterdam) **17**, 793 (1914).
[7] D. J. E. Callaway and D. J. Maloof, Phys. Rev. D **27**, 406 (1983); D. J. E. Callaway, *ibid.* **27**, 2974 (1983).
[8] R. C. Tolman, *The Principles of Statistical Mechanics* (Oxford University Press, London, 1938), Chap. 14.
[9] R. Evans *et al.*, Mol. Phys. **50**, 993 (1983).
[10] A. H. Narten and H. A. Levy, J. Chem. Phys. **55**, 2263 (1971).
[11] J. J. Jasper, J. Phys. Chem. Ref. Data **1**, 841 (1972).
[12] C. A. Croxton, *Introduction to Liquid State Physics* (Wiley, New York, 1975).
[13] H. Reiss, in *Advances in Chemical Physics*, edited by I. Prigogine (Interscience, New York, 1965), Vol. IX.
[14] J. P. M. Postma, J. H. C. Berendsen, and J. R. Haak, Faraday Symp. Chem. Soc. **17**, 55 (1982).
[15] A. J. Greenfield, J. Wellendorf, and N. Wiser, Phys. Rev. A **4**, 1607 (1971).
[16] P. W. Schmidt and C. W. Tompson, in *Simple Dense Fluids*, edited by H. Frisch (Academic, New York, 1968).
[17] F. P. Buff and R. A. Lovett, in *Simple Dense Fluids* (Ref. [16]).
[18] D. J. E. Callaway, Proteins: Struct. Func. Genetics **20**, 124 (1994).
[19] D. Chandler, Phys. Rev. E **48**, 2898 (1993).