Morphological Thermodynamics of Fluids: Shape Dependence of Free Energies

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We examine the dependence of a thermodynamic potential of a fluid on the geometry of its container. If motion invariance, continuity, and additivity of the potential are satisfied, only four morphometric measures are needed to describe fully the influence of an arbitrarily shaped container on the fluid. These three constraints can be understood as a more precise definition for the conventional term extensive and have as a consequence that the surface tension and other thermodynamic quantities contain, aside from a constant term, only contributions linear in the mean and Gaussian curvature of the container and not an infinite number of curvatures as generally assumed before. We verify this numerically in the entropic system of hard spheres bounded by a curved wall.

Although thermodynamics is built on extremely general assumptions, its implications are far reaching and powerful. One basic building block is geometry which has a long history in thermodynamics and statistical physics of condensed matter. The formulation of thermodynamics in terms of differential forms, scaled-particle theory (SPT) for fluids [1], depletion forces [2] of colloids in biological cells [3], and density functional theory (DFT) [4] based on fundamental geometric measures [5–7] are only a few examples of the importance of a general geometric point of view on thermodynamic properties. In Refs. [8–10] the structure and phase behavior of microemulsions was explained assuming that the free energy of the fluid on a mesoscopic scale is given solely by four fundamental geometric measures [11]. Here, we show numerically for the first time that these four fundamental measures are sufficient to describe accurately the free energy of a hard-sphere fluid in contact with a complexly shaped wall which supports the more general assumptions made in Refs. [8–11].

The grand potential $\Omega = \Omega[S; T, \mu]$ of a fluid depends on the temperature T and the chemical potential μ of the system, as well as on certain geometrical quantities which describe the shape of the container that bounds the system S. What are these thermodynamically relevant morphological parameters? One usually argues that every thermodynamic potential is an extensive quantity, which means that it scales linearly with the "size" of the system S. By partitioning a large system into identical smaller subsystems one normally assumes that $\Omega[S; T, \mu]$ is proportional to the volume $V = V[S]$ of the system and uses as ansatz $\Omega[S; T, \mu] = \omega(T, \mu)V[S]$. The intensive quantity $\omega(T, \mu)$ is the negative of the pressure $p(T, \mu)$ and is independent of the size of the confining container of S. This simple ansatz, however, is valid only for infinite bulk, i.e., "borderless" systems. If S is bounded by a container, Ω depends on the shape of the container in a potentially complicated manner and is conventionally described by an infinite expansion in powers of the cur-

vatures of the wall. However, we show that general considerations restrict this functional dependence on the shape to a linear combination of only four morphological measures, if all intrinsic (correlation) length scales are small compared to the system size. This finding is, in particular, important for systems such as porous media [12], biological cells [3], or complex fluids such as microemulsions [8] where fluids are confined by complexly shaped compartments and where the dependence of thermodynamic quantities and transport properties on the shape of pores or cells has significant functional and biological consequences. Our arguments, however, cannot be applied to critical phenomena, or if long ranged fluid-fluid or fluid-wall interactions are considered or if wetting or drying phenomena [13] occur at the wall, as intrinsic lengths in such systems have a macroscopic size.

Now we focus on the dependence of $\Omega[S]$ on the shape of the system S. The actual form of this mapping from a container onto a real number is given by the type and state of the fluid under consideration and is a complicated integral over the phase space of the system, which usually can be calculated only approximately. However, we impose three physical restrictions on this mapping.

(i) Motion invariance: The thermodynamic potential of a system must be independent of its location and orientation in space, i.e., $\Omega[gS] = \Omega[S]$ for all translations and rotations g in three dimensions.

(ii) Continuity: If a sequence of convex sets S_n converges towards the convex set S for $n \to \infty$, then $\Omega[S_n] \to \Omega[S]$. Intuitively, this continuity property expresses the fact that an approximation of a convex domain by, e.g., convex polyhedra also yields an approximation of the thermodynamic potential $\Omega[S]$ by $\Omega[S_n]$. In SPT it is shown that continuity is violated if the container S is very small and comparable in size to that of fluid particles [14]. Here we consider a larger container S.

(iii) Additivity: The functional of the union of two domains S_i, $i = 1, 2$, is the sum of the functional of the single domains subtracted by the intersection:

$\Omega[S_1 \cup S_2] = \Omega[S_1] + \Omega[S_2] - \Omega[S_1 \cap S_2]$. This relation generalizes the common rule for the addition of an extensive quantity for two disjunct domains $S_1 \cap S_2 = \varnothing$ to the case of overlapping domains by subtracting the value of the thermodynamic quantity of the double-counted intersection. Note that the intersection $S_1 \cap S_2$ does not need to be a volume but can rather be an area or a line for adjacent containers S_i. Additivity can break down if long ranged interactions are present or if the system develops a macroscopic intrinsic length scale. A fluid can be considered additive even inside a concave container, if opposing walls are separated by several correlation lengths.

Naturally the question arises about the most general form of a potential that satisfies these three conditions. The Hadwiger theorem [15,16] states that every motion-invariant, continuous, and additive functional in three dimensions can be written as a linear combination of the volume $V = \int_S dV$, the surface area $A = \int_{\partial S} dA$, the integrated mean curvature $C = \int_{\partial S} H dA$, and the Euler characteristic $X = \int_{\partial S} K dA$ of the container. Therefore we write

$$\Omega[S] = -pV[S] + \sigma A[S] + \kappa C[S] + \bar{\kappa} X[S] \quad (1)$$

as a *complete* expression for the grand canonical potential, if the aforementioned conditions are satisfied [8–11]. The pressure $p(T, \mu)$, the surface tension at the planar wall $\sigma(T, \mu)$, and the bending rigidities $\kappa(T, \mu)$ and $\bar{\kappa}(T, \mu)$ are properties of the fluid and the wall-fluid interaction, but are independent of the actual shape of the bounding wall. The latter two thermodynamic coefficients describe the influence of the curvature of the wall. Similar coefficients are also used for the Helfrich Hamiltonian [17], which describes the free energy cost of bending a membrane. It is compatible with Eq. (1) on a length scale larger than the persistence length of the membrane, where renormalized contributions proportional to H^2 vanish due to thermal fluctuations.

Note that Eq. (1) can easily be applied even to complexly shaped objects because the shape of S enters Ω only via the four simple morphometric measures V, A, C, and X, while the thermodynamic coefficients σ, κ, and $\bar{\kappa}$ can be determined in a simple geometry.

Thermodynamic quantities can be derived directly from Ω and inherit a simple dependence on the shape of S by virtue of Eq. (1). The interfacial tension $\gamma = (\Omega + pV)/A$, which measures the total change in the grand potential per unit area introduced by the wall, can be evaluated using

$$\gamma = \sigma + \kappa \bar{H} + \bar{\kappa} \bar{K}, \quad (2)$$

where $\bar{H} = C/A$ and $\bar{K} = X/A$ are the averaged mean and Gaussian curvatures of the bounding wall. These geometrical quantities can be calculated from the principal radii of curvature R_1 and R_2 via $H = (1/R_1 + 1/R_2)/2$ and $K = 1/(R_1 R_2)$. Note that this further justifies the ansatz used in SPT [1,18] for the interfacial tension and shows

that the analytic dependence of γ on the curvature is a direct consequence of the additivity of the grand potential. No higher powers or derivatives of $\bar{H}$ or $\bar{K}$ contribute either to γ or to Ω.

Closely related to the interfacial tension is Γ, the excess (over the bulk) amount of fluid adsorbed at the wall per unit area, which is defined as $\Gamma \equiv (1/A) \int_S [\rho(\mathbf{r}) - \rho] dV$, where ρ is the bulk density and $\rho(\mathbf{r})$ is the inhomogeneous density distribution of the fluid. It inherits the morphometric form of the interfacial tension via Gibbs' adsorption theorem

$$-\Gamma = \left(\frac{\partial \gamma}{\partial \mu} \right)_{T,V} = \frac{\partial \sigma}{\partial \mu} + \frac{\partial \kappa}{\partial \mu} \bar{H} + \frac{\partial \bar{\kappa}}{\partial \mu} \bar{K}. \quad (3)$$

If a fluid is bounded by a container one denotes the number density closest to the wall as contact density ρ^c, which becomes $\bar{\rho}^c$, when averaged over the boundary surface. For hard walls $\bar{\rho}^c$ can be regarded as a thermodynamic quantity because of an exact sum rule [18,19] and also features a simple dependence on the geometry:

$$\bar{\rho}^c = p + 2\sigma \bar{H} + \kappa \bar{K}. \quad (4)$$

This relation can be derived by generalizing the arguments given by Henderson [19]. Note that the density distribution of the fluid away from contact depends in a more complicated way on the curvature of the wall.

We test the vanishing of higher powers of $\bar{H}$ and $\bar{K}$ in thermodynamic quantities such as Ω, γ, Γ, or $\bar{\rho}^c$ by extensive numerical studies of a fluid of hard spheres of radius R bounded by a hard wall using DFT. For a given chemical potential μ, the bulk number density ρ of spheres or equivalently the packing fraction $\eta = 4\pi R^3 \rho/3$ are fixed. Hard-core interactions do not introduce an energy scale such that we can account for the temperature dependence of all thermodynamic quantities by scaling energies with $\beta = 1/(k_B T)$. One can expect the grand potential of a hard-sphere fluid to be additive as hard-core interactions are short ranged and the correlation length remains small in the fluid phase. Unfortunately, for arbitrarily shaped walls, there exists no reliable and accurate direct method to calculate thermodynamic quantities. However, for simple geometries such as planar, spherical, or cylindrical walls, it is possible to apply, e.g., DFT techniques [4], which allow the calculation of σ, κ, and $\bar{\kappa}$. For these geometries, the curvatures and the contact density are constants over the surface such that we can replace averages over the surface by their local quantities. Rosenfeld's fundamental measure theory (FMT) [5] and the White-Bear version of FMT [6,7] have proven to describe the thermodynamics and structure of hard-sphere fluids very accurately, and both give qualitatively equivalent results in the following analysis, as well as the non FMT-based Tarazona Mark I functional [20]. It is important to realize that minimizing a FMT functional does not restrict the results to standard SPT behavior [18].

The thermodynamic coefficients of Eq. (1) are shown in Fig. 1 as functions of the packing fraction η of the fluid. As a dividing interface, which determines the surface area A as well as the curvatures H and K, we choose the surface where the contact density is measured. From these coefficients one can obtain values for γ and ρ^c for various geometries. In the inset of Fig. 1 we show the relative error (full line) of γ of a hard-sphere fluid with packing fraction $\eta = 0.3$ at a cylinder with radius R_c as calculated with the thermodynamic coefficients compared to that obtained directly from DFT. This relative error is of the same order of magnitude as the relative numerical error of the contact sum rules, Eq. (4), indicating clearly that the very small deviation between the morphometric interfacial tension and that from a direct DFT calculation is a numerical error of our calculation.

In order to show that the linear expansion in H and K of γ and ρ^c is sufficient, we include for the analysis of our data also nonadditive terms and show that they do not contribute either to γ or to ρ^c. To this end we introduce the curvature expansion of, e.g., the contact density

$$\rho^c = \rho_P^c + \rho_H^c H + \rho_K^c K + \rho_{H^2}^c H^2 + \rho_{HK}^c HK$$
$$+ \rho_{H^3}^c H^3 + \mathcal{O}(R_{1,2}^{-4}). \tag{5}$$

The coefficients ρ_ξ^c for $\xi = P, H, K, H^2, HK, H^3, \dots$ can be determined numerically using DFT. The results in Fig. 2 show that irrespective of the bulk density only the additive terms ρ_P^c, ρ_H^c, and ρ_K^c contribute to ρ^c.

Note that, in particular, ρ_K^c (additive) contributes to the contact density, whereas $\rho_{H^2}^c$ (nonadditive) does not, although both K and H^2 feature the same quadratic dependence on the radii of curvature. This shows that the expansion in H and K is complete and not a truncated power series. In the inset of Fig. 2 we show the relative error of the contact density of a hard-sphere fluid at a sphere with radius $5R$ as a function of η obtained by the morphometric form (dashed line) of ρ^c, Eq. (4), and by the generalized curvature expansion (full line), Eq. (5), both compared to the direct calculation of DFT. Since in both cases the relative error is roughly the same, we conclude that additive contributions are sufficient to describe the influence of curvature on the contact density ρ^c.

To further highlight that the remarkably simple functional dependence on only four morphometric measures of the container is a peculiar feature of thermodynamic quantities, we introduce, in addition to the hard-wall potential, a short-ranged *soft* part to the wall-fluid potential of the form $V_{\text{soft}}(u) = V_0 \exp(-u/\lambda)$, where u denotes the normal distance from the dividing interface. It can be either attractive, if $V_0 < 0$, or repulsive, if $V_0 > 0$. Note that this additional part of the wall-fluid interaction leaves the morphometric form of thermodynamic quantities such as the grand potential Ω, Eq. (1), and the surface tension γ, Eq. (2), unchanged. The contact density ρ^c, however, loses its morphometric form for any nonzero value of V_0 because the sum rule Eq. (4) acquires an additional term [19].
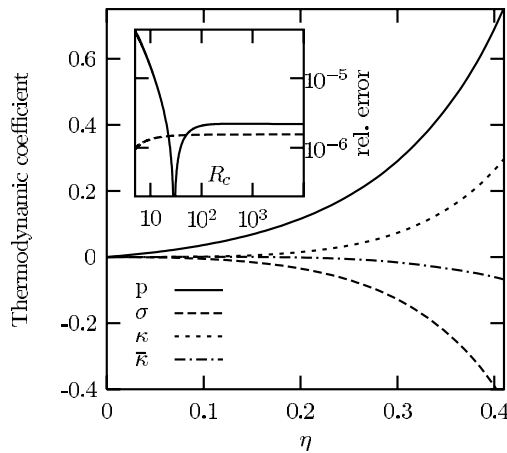

FIG. 1. The expansion coefficients as defined in Eq. (1) of the grand potential of a hard-sphere fluid. For each value of η, the four thermodynamic coefficients can be used to calculate thermodynamic quantities for arbitrarily shaped systems. The solid line of the inset shows the relative error of γ at a cylinder with radius R_c calculated using the thermodynamic coefficients at $\eta = 0.3$. This error can be compared to the numerical relative error for a sum rule [18,19] (dashed line), which gives an estimate for the accuracy of our DFT data. Both errors are of the same order of magnitude such that our numerical data are in agreement with the prediction of Eq. (1). The fluid was modeled via Rosenfeld's FMT [5].
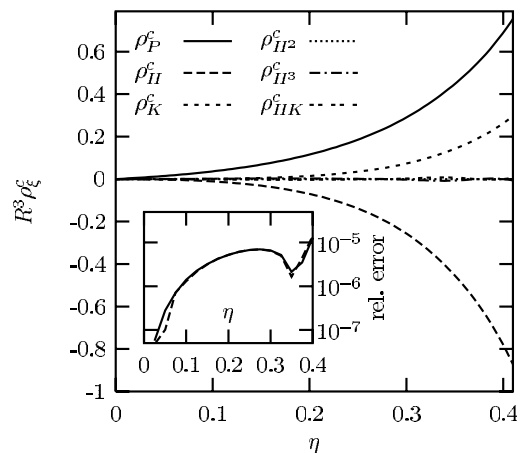

FIG. 2. Curvature expansion coefficients for the contact density of a hard-sphere fluid as a function of the packing fraction η. Only the additive contributions ρ_P^c, ρ_H^c, and ρ_K^c contribute. The inset shows the relative error for the contact density at a spherical container with radius $5R$ between a direct DFT calculation and two approaches: For the solid curve all shown curvature expansion coefficients are used, for the dashed one only additive contributions. The error, which is due to the numerical inaccuracies, is in both cases roughly the same. This shows that nonadditive terms do not contribute to the thermodynamic quantity ρ^c. Similar results were found for γ (Fig. 1).
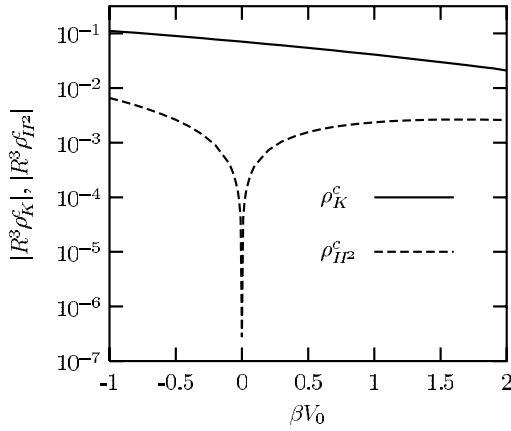
FIG. 3. If the external potential of a hard container is perturbed by an additional potential as, e.g., $V_{soft}(u) = V_0 \exp(-u/\lambda)$ the contact density ρ^c is no longer a thermodynamic quantity for $V_0 \neq 0$. In this case nonadditive contributions such as $\rho^c_{H^2}$ are necessary to describe the dependence on the curvatures of the wall. Here we show ρ^c_K and $\rho^c_{H^2}$ in a logarithmic plot for $\lambda = R$ and a packing fraction $\eta = 0.3$. It is striking that even very small perturbations lead to $\rho^c_{H^2} \neq 0$ which is a clear indication that additivity of the contact density ρ^c is destroyed. In contrast, ρ^c_K contributes to the contact density for all V_0.

This effect can be demonstrated by performing a curvature expansion, Eq. (5), of the contact density as a function of V_0. In the case of a purely hard wall, $V_0 = 0$, the curvature expansion contains only additive contributions (ρ^c_P, ρ^c_H, and ρ^c_K), whereas for nonzero values of V_0 this is no longer the case and the amplitude of, e.g., $\rho^c_{H^2}$, increases with an increasing value of $|V_0|$. As an example of this behavior we display in Fig. 3 ρ^c_K (additive) and $\rho^c_{H^2}$ (nonadditive) for a hard-sphere fluid with packing fraction $\eta = 0.3$ for values of βV_0 from -1 to 2 and $\lambda = R$. It is very striking that already for very small amplitudes $|V_0| \neq 0$, for which the soft part of the wall-fluid interaction can be regarded as a small perturbation, the contact density ρ^c acquires additional nonadditive contributions. We verified that the interfacial tension γ keeps its morphometric form (not shown), as expected.

Monte Carlo simulation confirms that the contact density of a hard-sphere fluid with $\eta = 0.3314$ around a biaxial ellipsoid with half axes $(4, 4, 10)R$ as obtained by Eq. (4). Within the statistical errors of the simulation (about 1%), the results of Eq. (4) together with the thermodynamic coefficients shown in Fig. 1 agree with the simulation data [21]. Furthermore, we also confirmed that Eq. (2) holds accurately in concave geometries if the perturbations introduced by the container do not interfere at caustic points. For a relatively high packing fraction of hard spheres of $\eta = 0.4$ the deviation between Eq. (2) and direct DFT results is smaller than 1.5% for all radii of the cylinder larger than $5R$.

We presented a more precise definition than the conventional term "extensive" to describe the dependence of a thermodynamic quantity of a fluid with short intrinsic length scales on the shape of the system. The assumption that the grand potential of a fluid is motion invariant, continuous, and additive allows an expansion in terms of only four simple morphological functionals [8–11]. As a consequence, the curvature expansion for thermodynamic quantities terminates after linear terms in mean and Gaussian curvatures. This observation allows a calculation of thermodynamic quantities for complexly shaped objects with a greatly reduced effort in comparison to direct methods. The ideas presented here and tested numerically for the hard-sphere fluid should be applicable also to fluids with short-ranged interactions provided that intrinsic length scales are small compared to typical features of the container. If, however, length scales are comparable, continuity or additivity may be violated and thermodynamic quantities acquire additional contributions. The present approach is currently being extended to include local structure (density profiles) which will allow the prediction of entropic contributions to the effective interactions of complicated macromolecules.

[1] H. Reiss, H. L. Frisch, E. Helfand, and J. L. Lebowitz, J. Chem. Phys. **32**, 119 (1960).
[2] R. Roth, R. Evans, and S. Dietrich, Phys. Rev. E **62**, 5360 (2000).
[3] R. J. Ellis, Trends Biochem. Sci. **26**, 597 (2001).
[4] R. Evans, Adv. Phys. **28**, 143 (1979).
[5] Y. Rosenfeld, Phys. Rev. Lett. **63**, 980 (1989).
[6] R. Roth, R. Evans, A. Lang, and G. Kahl, J. Phys. Condens. Matter **14**, 12 063 (2002).
[7] Y.-X. Yu and J. Wu, J. Chem. Phys. **117**, 10 165 (2002).
[8] C. N. Likos, K. R. Mecke, and H. Wagner, J. Chem. Phys. **102**, 9350 (1995).
[9] K. Mecke, J. Phys. Condens. Matter **8**, 9663 (1996).
[10] K. Mecke, Fluid Phase Equilib. **150/151**, 591 (1998).
[11] K. R. Mecke, *Integralgeometrie in der Statistischen Physik* (Harri Deutsch, Frankfurt, Germany, 1994).
[12] C. H. Arns, M. A. Knackstedt, and K. R. Mecke, Phys. Rev. Lett. **91**, 215506 (2003).
[13] R. Evans, R. Roth, and P. Bryk, Europhys. Lett. **62**, 815 (2003).
[14] H. Reiss, H. L. Frisch, and J. L. Lebowitz, J. Chem. Phys. **31**, 369 (1959).
[15] H. Hadwiger, *Vorlesungen über Inhalt, Oberfläche und Isoperimetrie* (Springer, Berlin, Germany, 1957).
[16] K. R. Mecke, Int. J. Mod. Phys. B **12**, 861 (1998).
[17] W. Helfrich, Z. Naturforsch. **28C**, 693 (1973).
[18] P. Bryk, R. Roth, K. R. Mecke, and S. Dietrich, Phys. Rev. E **68**, 31 602 (2003).
[19] J. R. Henderson, Mol. Phys. **50**, 741 (1983).
[20] P. Tarazona, Mol. Phys. **52**, 81 (1984).
[21] P. Bryk (private communication).