LETTER TO THE EDITOR

Dimensional crossover and the freezing transition in density functional theory

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Abstract. A modified geometrically based free-energy functional for hard spheres is proposed which gives reliable results even for situations of extreme confinements that reduce the effective dimensionality D. It is accurate for hard spheres between narrow plates ($D = 2$), inside narrow cylindrical pores ($D = 1$), and is *exact* in the 0D limit (a cavity that cannot hold more than one particle). This functional also predicts the hard-sphere fluid–solid transition in excellent agreement with the simulations.

The density functional formalism is one of the most successful and widely applicable approaches to a variety of interfacial phenomena such as adsorption, wetting, and freezing, and enables one to investigate confined fluids with all sorts of inhomogeneities [1, 2]. Situations which may be termed as quasi-2D (fluids between two narrow plates), quasi-1D (fluids inside narrow cylindrical pores), and quasi-0D (cavities that cannot hold more than one particle) are generated by external potentials acting on the fluid that reduce its effective dimensionality, D. Spatial confinements drastically affect structural and dynamical quantities as well as the location of phase transitions. The density profile exhibits sharp peaks corresponding to microscopic layers of the liquid, the viscosity is observed to increase drastically [3], and the location of the freezing transition [4, 5], the glass transition [6] and the triple point [7] shift significantly with respect to their bulk values.

The exact 3D free-energy functional of the average one-body density, $\rho(r)$, should be able to provide a unifying description of all such confined situations within density functional theory. The central quantity is the excess free energy (over the exactly known 'ideal-gas' contributions), $F_{ex}[\rho(r)]$, which originates in interparticle interactions, and is generally unknown! Hence, the requirement of obtaining a realistic lower-dimensional functional by shrinking the dimensionality of the system is an important consistency check of any approximate functional. This consistency is especially important if the 3D functional is invoked to describe situations of extremely confined fluids [8, 9].

The well studied hard-sphere fluid serves as the almost standard reference system [10] for classical fluids, and provides an important test for all density functional approximations. The minimal prerequisite for the 3D functional, to have at least gross similarity to the exact

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values in lower-effective-dimensionality situations, was first achieved via the smoothed density approximation [11]. Many functionals of comparable, sometimes better, accuracy were subsequently developed [1], which could provide qualitative, sometimes quantitative, agreement with simulated density profiles of confined fluids. The exact functional for 1D spheres (hard rods), due to Percus [12], provided an important paradigm. Most of these functionals were also able to exhibit a freezing transition for the hard spheres, with melting and freezing densities in reasonable agreement with simulations [13, 14]. But none of these functionals could feature the exact 0D [15] limit, or the exact bulk 1D [12] limit. Functionals built upon the bulk 3D data as essentially numerical input do not contain the building blocks for achieving these limits.

A fundamental-measure free-energy model [16–22], on the other hand, derives the uniform (bulk) fluid properties as a special case, rather than employing them as input. The simplest such functional [17] proved very successful for 3D fluids in the bulk and in slit-like pores, but it was unsuitable for describing the solid [17, 20, 23–25]. In this letter we analyse its behaviour for different effective dimensionalities ($D = 2, 1, 0$) by applying confining external potentials to the 3D bulk fluid. We modified the form of the functional so that it reproduces the exact 0D limit. As a result it gives accurate results for the 3D fluid–solid transition, and becomes generally reliable in situations of extreme confinements. A detailed account of the present work will be submitted for publication elsewhere [26].

To simplify the notation and discussion we shall consider specifically the single-component system of hard spheres of radius R. The fundamental-measure excess-free-energy functional was postulated [17] to have the following form:

$$\frac{F_{ex}[\{\rho(\boldsymbol{r})\}]}{k_B T} = \int \mathrm{d}\boldsymbol{x} \; \Phi[\{n_\alpha(\boldsymbol{x})\}] \tag{1}$$

where it is assumed that Φ is a function of the following six weighted densities:

$$n_\alpha(\boldsymbol{x}) = \int \rho(\boldsymbol{x}')w^{(\alpha)}(\boldsymbol{x} - \boldsymbol{x}') \; \mathrm{d}\boldsymbol{x}'$$

which are *dimensional* quantities. The weight functions $w^{(\alpha)}$, $\alpha = 3, 2, 1, 0, V2, V1$, are [17] characteristic functions for the geometry of the sphere: two scalar functions, representing the characteristic functions for the volume and the surface of a particle, $w^{(3)}(r) = \Theta(R - r)$, $w^{(2)}(r) = \delta(R - r)$, and a vector function $\boldsymbol{w}^{(V2)}(r) = \boldsymbol{r}/r\delta(R - r)$; the other three weights are simply proportional:

$$w^{(0)}(\boldsymbol{r}) = \frac{w^{(2)}(\boldsymbol{r})}{4\pi R^2} \qquad w^{(1)}(\boldsymbol{r}) = \frac{w^{(2)}(\boldsymbol{r})}{4\pi R} \qquad \boldsymbol{w}^{(V1)}(\boldsymbol{r}) = \frac{\boldsymbol{w}^{(V2)}(\boldsymbol{r})}{4\pi R}.$$

The weighted densities $n_\alpha(\boldsymbol{x})$ provide a functional basis set, $\{\phi_j\}$, for expanding the function $\Phi = \sum_i A_i(n_3)\phi_i$, of dimension (volume)$^{-1}$. By including only the five positive power combinations of the weighted densities, $\{\phi_j\} = n_0, n_1 n_2, \boldsymbol{n}_{V1} \cdot \boldsymbol{n}_{V2}, n_2^3, n_2(\boldsymbol{n}_{V2} \cdot \boldsymbol{n}_{V2})$, the following 3D excess free-energy density was derived [17, 20]:

$\Phi[\{n_\alpha\}] = \Phi_1 + \Phi_2 + \Phi_3$

$$\Phi_1 = -n_0 \ln(1 - n_3) \qquad \Phi_2 = \frac{n_1 n_2 - \boldsymbol{n}_{V1} \cdot \boldsymbol{n}_{V2}}{1 - n_3} \qquad \Phi_3 = \frac{\frac{1}{3}n_2^3 - n_2(\boldsymbol{n}_{V2} \cdot \boldsymbol{n}_{V2})}{8\pi(1 - n_3)^2}. \tag{2}$$

This free-energy model unifies the Percus–Yevick [27] and scaled-particle [28] theories. The bulk direct correlation function, as obtained from the second functional derivative of this functional, is identical to the analytic solution of the Percus–Yevick equation [27, 29].

Density profiles obtained from this functional for the fluid in confinement situations between 'quasi-2D' and 'quasi-3D' (e.g. slit-like pores of various widths) are in very good agreement with the simulations [16–22, 23–25]. It also gives an accurate free energy in the 2D limit, but it has negative divergence in the 1D limit, and it cannot stabilize the solid in coexistence with the liquid [17, 20, 23–25].

In order to improve the dimensional crossover behaviour of the functional equation (2), let us consider in more detail the contributions of the different components, Φ_1, Φ_2, Φ_3. In the 1D-limit, $\rho(x, y) = \rho^{(1D)}\delta(x)\delta(y)$, where $\rho^{(1D)} = N/L$ is the 1D density and $\eta = 2\rho^{(1D)}R$ is the 1D packing fraction, Φ_3 yields a non-integrable singularity [24, 20]. Yet $\Phi_{1+2} = \Phi_1 + \Phi_2$ (i.e. eliminating Φ_3) yields [20] the *exact* excess free energy of the bulk hard-rod system, and [26] remarkably also the corresponding *exact* direct correlation function.

The quasi-0D situation for hard spheres of any number of dimensions is achieved via an external potential such that there is a cavity which cannot hold more than one particle. The 0D packing fraction is the average occupation of the cavity, $\eta = N \leqslant 1$, and there is an excess free energy

$$f^{(0D)} = \frac{F_{ex}}{k_B T} = \eta + (1 - \eta)\ln(1 - \eta)$$

independent of the confining potential [15]. We now try to recover this result as the ultimate crossover for any density functional. In the 0D limit, $\rho(r) = \eta\delta(r)$, the first term Φ_1 is directly integrated to give the exact $f^{(0D)}$ via a change of variables, $\tau = 1 - n_3(x)$ and $d\tau = -n_0(x)\,dx$. In this limit $n_{V1}(r) \cdot n_{V2}(r)$ and $n_1(r) \cdot n_2(r)$ become equal, and they diverge at $|r| = R$. The 'anti-symmetric' form of Φ_2 cancels out these diverging terms exactly. However, Φ_3 does not possess such an anti-symmetry, and gives a strong negative divergence. This is why the functional equation (2) overstabilized the solid with respect to the fluid.

Thus, a simple way to achieve the exact 0D limit is to modify Φ_3 in such a way that the diverging terms cancel each other, preserving at the same time of all the favourable features of the functional in the 3D situations. We therefore propose the following *new* form for the third term:

$$\Phi_3^{(new)} = \left[\frac{\frac{1}{3}(n_2)^3}{8\pi(1 - n_3)^2}\right](1 - \xi^2)^3 \tag{3}$$

where $\xi(r) \equiv |n_{V2}(r)/n_2(r)|$. From

$$(n_2)^3(1 - \xi^2)^3 = (1/n_2)^3((n_2)^2 - n_{V2}(r) \cdot n_{V2}(r))^3$$

one directly observes that $\Phi_3^{(new)}$ vanishes in the 0D limit since $n_1(r)n_2(r) - n_{V1}(r) \cdot n_{V2}(r) \to 0$ and $1/n_2(r) \to 0$ at $|r| = R$. The form equation (3), which is a key result of this letter, was chosen since it recovers Φ_3 by the first two terms, $1 - 3\xi^2$, in its ξ^2-expansion of $(1 - \xi^2)^3$, and thus it also yields the Percus–Yevick pair direct correlations for the bulk fluid. Since it does not have a term of order ξ^3, the new form, equation (3), yields the same three-particle bulk direct correlation functions as the original one in equation (2), but higher-order direct correlation functions do differ from those obtained from the original functional. The new form, equation (3), is within the original fundamental-measure description, and just corresponds to some enlargement of the basis set, $\{\phi_j\}$.

This anti-symmetrized form, suggested by the 0D limit, also improves the functional near the bulk 3D limit. For example, the thermodynamic consistency of the bulk pair correlations obtained by using the *bridge* functional [20, 16], derived from the free-energy functional with the new $\Phi_3^{(new)}$ is much better than that obtained with Φ_3. In 2D situations

it performs about as well as Φ_3. The contribution of the new $\Phi_3^{(new)}$ does not strictly vanish in the bulk 1D limit, as required to give the exact result, but it is generally very small. We re-emphasize that, by construction, the 0D limit is reproduced exactly.

Finally let us consider the 3D freezing transition. In the hard-sphere solid the particles can be viewed as confined in a fluctuating almost spherical cage of its nearest neighbours. This kind of confinement is very similar to that achieved by the 0D limit. Hence, any free-energy functional which attempts to describe the solid correctly should simultaneously provide reliable results for the 0D limit. This important interconnection was ignored by all previous density functional studies of the hard-sphere freezing, but it is automatically incorporated by our new functional. If one approximates the solid by a superposition of *normalized* narrow Gaussians, then it can be stabilized by any functional that is able to achieve *gross similarity* with the exact result for $\eta = 1$ in the 0D limit. This explains why such a large class of disparate free-energy functionals was able to provide a reasonable description of the freezing transition parameters. However, because these functionals could not yield the exact 0D limit, none of them could yield the correct vacancy concentration of the solid. In addition, none of these functionals featured the correct divergence of the equation of state of the solid at closest packing for the fcc lattice.

Due to its remarkable 0D properties, our new functional is the first that can yield the solid with the correct vacancy concentration (i.e. without assuming *a priori* the normalization of the Gaussians). With $\Phi_3^{(new)}$ we can obtain excellent solid–fluid transition parameters when compared with simulations (simulation results [13, 14] are given hereafter in parentheses): the packing fraction of the fluid, $\eta_F = 0.491$ (0.494), and the solid, $\eta_S = 0.540$ (0.545), the melting pressure, $P\sigma^3/k_BT = 12.3$ (11.7), the Lindemann ratio, $L = 0.101$ (0.129), and the vacancy concentration, $e^{-17.1}$ (≈ 0). We also obtain an excellent equation of state for the fcc hard-sphere solid, including the correct divergence at closest packing. More detailed results will be presented elsewhere [26]. We have indications that further improvements of the 2D and 1D limits can be achieved by including also slightly more complicated (e.g., tensorial) forms of ξ in Φ_3. The analysis of the fundamental-measure theory as applied to parallel hard cubes [30] should prove useful. The understanding of the special role played by the fundamental-measure functional, derived from 'liquid' considerations, for the correct description of the solid, may also lead to a better understanding of the density functional theory of freezing. Pending further progress along these lines, our result, using $\Phi_3^{(new)}$, provides the first comprehensive free-energy functional for 3D hard-sphere fluids with adequate properties of dimensional crossover.

References

[1] See the following collection of reviews:
Henderson D (ed) 1992 *Fundamentals of Inhomogeneous Fluids* (New York: Dekker)
and in particular the review by R Evans.

[2] Löwen H 1994 *Phys. Rep.* **237** 249
[3] Klafter J and Drake J M (ed) 1989 *Molecular Dynamics in Restricted Geometries* (New York: Wiley)
[4] Christenson H K 1995 *Phys. Rev. Lett.* **74** 4675
[5] Schmidt M and Löwen 1996 *Phys. Rev. Lett.* **76** 4552
[6] See, e.g.,
    Fehr T and Löwen H 1995 *Phys. Rev.* E **52** 4016
[7] Duffy J A, Wilkinson N J, Fretwell H M, Alam M A and Evans R 1995 *J. Phys.: Condens. Matter* **7** L713
[8] Patra C N and Ghosh S K 1994 *Phys. Rev.* **50** 5123
[9] Peterson B K, Gubbins K, Heffelfinger G S, Marini Bettolo Marconi U and van Swol F 1988 *J. Chem. Phys.*
    88 6487
[10] Hansen J P and McDonald I R 1986 *Theory of Simple Liquids* 2nd edn (London: Academic)
[11] Tarazona P 1984 *Mol. Phys.* **52** 81; 1985 *Phys. Rev.* A **31** 2672
[12] Percus J K 1976 *J. Stat. Phys.* **15** 505
[13] See, e.g., the review by
    Baus M 1990 *J. Phys.: Condens. Matter* **2** 2241
[14] Ohnesorge R, Löwen H and Wagner H 1993 *Europhys. Lett.* **22** 245; 1994 *Phys. Rev.* E **50** 4801
[15] Consider hard spheres in any number of dimensions confined inside a cavity that cannot hold more than
    one particle. The canonical partition function is Z_1 for $N = 1$ and $Z_{N \geqslant 2} = 0$. The grand partition
    function is $\Xi = \sum_{N=0}^{\infty} (Z_N / N!) \mathrm{e}^{\beta\mu N} = 1 + Z_1 \mathrm{e}^{\beta\mu}$, $N = (\partial/\partial\beta\mu) \ln \Xi$, $\beta P = \ln \Xi$, so the free energy
    is $\beta F = -\beta P + \beta\mu N = \ln(1 - N) + N \ln[N/Z_1(1 - N)]$. For ideal particles with no restriction on
    occupation of the cavity $Z_N = (Z_1)^N$, and $\Xi = \exp(Z_1 \mathrm{e}^{\beta\mu})$, so $\beta F^{id} = -N + N \ln(N/Z_1)$ and thus
    $\beta(F - F^{id}) = N + (1 - N) \ln(1 - N)$.
[16] Rosenfeld Y 1996 *Chemical Applications of Density-Functional Theory (ACS Symposium Series 629)* ed B
    Laird, R Ross and T Ziegler (Washington, DC: ACS Publishing)
[17] Rosenfeld Y 1989 *Phys. Rev. Lett.* **63** 980
[18] Rosenfeld Y, Levesque D and Weis J J 1990 *J. Chem. Phys.* **92** 6818
    Rosenfeld Y 1990 *J. Chem. Phys.* **93** 4305
[19] Rosenfeld Y 1990 *Phys. Rev.* A **42** 5978
[20] Rosenfeld Y 1993 *J. Chem. Phys.* **98** 8126; 1996 *Phys. Rev.* E at press
[21] Rosenfeld Y 1994 *Phys. Rev.* E **50** R3318; 1995 *Mol. Phys.* **86** 637
[22] Rosenfeld Y 1994 *Phys. Rev. Lett.* **72** 3831; 1995 *J. Phys. Chem.* **99** 2857
[23] Kierlik E and Rosinberg M L 1990 *Phys. Rev.* A **42** 3382
[24] Kierlik E and Rosinberg M L 1991 *Phys. Rev.* A **44** 5025
[25] Phan S, Kierlik E, Rosinberg M L, Bildstein B and Kahl G 1993 *Phys. Rev.* E **48** 618
[26] Rosenfeld Y, Schmidt M, Löwen H and Tarazona P 1996 to be published
[27] Percus J K and Yevick G J 1958 *Phys. Rev.* **110** 1
    Lebowitz J L 1964 *Phys. Rev.* A **133** 895
[28] Reiss H, Frisch H and Lebowitz J L 1959 *J. Chem. Phys.* **31** 369
    Reiss H 1992 *J. Phys. Chem.* **96** 4736
[29] Rosenfeld Y 1988 *J. Chem. Phys.* **89** 4272
[30] Cuesta J A 1996 *Phys. Rev. Lett.* **76** 3742