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Density-functional theory of classical systems*

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An exact density-functional theory is developed for nonuniform classical systems, expressing the free energy in terms of direct correlation functions. It is shown how this theory may be used in a practical fashion to remove several unjustified, although physically plausible, approximations made in earlier work. Further understanding of the approximations is obtained.

In a recent article[1] the authors, together with Stroud, presented an approximate density-functional theory capable of predicting from first principles the particle density $n(\vec{r})$ at position $\vec{r}$ and the Helmholtz free energy for simple, nonuniform, classical fluids subjected to an external potential. The sole input, aside from several physically motivated approximations, was the intermolecular two-body interaction which was taken to be a Lennard-Jones (6-12) potential. The theory was applied to liquid argon with a free surface, yielding good results for the surface tension over a wide range of temperatures and physically reasonable results for the (as yet unmeasured) density in the vicinity of the liquid-gas interface. The theory also produced sensible results for liquid argon pressed against a model container wall in that it predicts oscillations in the density near the wall, the amplitude of the oscillations increasing with the pressure.

Despite the success of the theory, several approximations made in formulating it are certainly open to question.[2] It is the purpose of this work to develop a formally exact density-functional theory and to indicate how this exact theory may be used in a practical fashion to eliminate the most questionable approximations used in Ref. 1. Also, the nature and validity of these approximations is clarified by the present work.

Consider a classical system of particles with fixed chemical potential μ and temperature T in the presence of an external potential $v(\vec{r})$ which couples to the particle number density $n(\vec{r})$. Then according to Mermin,[3] there exists a functional $\tilde{\Omega}[n]$ of $n(\vec{r})$ such that the minimum value of

$$\Omega \equiv \tilde{\Omega}[n] + \int d^3r\, v(\vec{r})n(\vec{r}) , \tag{1}$$

with respect to variation of $n(\vec{r})$ at constant μ, T, $v(\vec{r})$, and volume V, is the equilibrium grand free energy of the system; $n(\vec{r})$ at the minimum is the equilibrium number density. The equation determining the minimum is

$$\left.\frac{\delta\Omega}{\delta n(\vec{r})}\right|_{T,\mu,v(\vec{r}),V} = -v_n(\vec{r}) + v(\vec{r}) = 0 , \tag{2}$$

where

$$v_n(\vec{r}) \equiv -\left.\frac{\delta\tilde{\Omega}[n]}{\delta n(\vec{r})}\right|_{T,\mu,V} . \tag{3}$$

We remark that, for any given $n(\vec{r})$, $v_n(\vec{r})$ is simply the external potential which would produce that particle density.

Let us define the direct correlation function $C(\vec{r},\vec{r}')$ in the usual[4] manner:

$$\frac{\delta v_n(\mathrm{r})}{\delta n(\vec{r}')} \equiv -\beta^{-1}\left[\frac{\delta(\vec{r}-\vec{r}')}{n(\vec{r})} - C(\vec{r},\vec{r}')\right] , \tag{4}$$

where $\beta^{-1} = k_BT$, k_B being Boltzmann's constant. Further, the pair correlation function $h(\vec{r},\vec{r}')$ is defined by

$$\frac{\delta n(\vec{r})}{\delta v_n(\vec{r}')} = -\beta n(\vec{r})[\delta(\vec{r}-\vec{r}') + n(\vec{r}')h(\vec{r},\vec{r}')] . \tag{5}$$

Combination of (4) and (5) with the identity

$$\int d^3r''\, \frac{\delta n(\vec{r})}{\delta v_n(\vec{r}'')}\, \frac{\delta v_n(\vec{r}'')}{\delta n(\vec{r}')} = \delta(\vec{r}-\vec{r}') \tag{6}$$

yields the Ornstein-Zernike relation[4]

$$h(\vec{r},\vec{r}') = C(\vec{r},\vec{r}') + \int d^3r''\, h(\vec{r},\vec{r}'')n(\vec{r}'')C(\vec{r}'',\vec{r}') \tag{7}$$

for nonuniform systems.

Next, suppose that we have some means of obtaining $C(\vec{r},\vec{r}')$ given an arbitrary, but physically reasonable, density $n(\vec{r})$. We would then want to functionally integrate (4) to obtain $v_n(\vec{r})$. This integration will take the system from some initial density $n_0(\vec{r})$ to a final density $n(\vec{r})$. Following

Lebowitz and Percus,[5] we choose a path in the space of density functions which is characterized by a single parameter α which varies from 0 to 1. Then the integration gives

$$\beta[v_n(\vec{r}) - v_0(\vec{r})] = -\ln[n(\vec{r})/n_0(\vec{r})] + \int_0^1 d\alpha \int d^3r' \, \frac{\partial n(\vec{r}\,';\alpha)}{\partial \alpha} \times C(\vec{r},\vec{r}\,';\alpha) . \tag{8}$$

The particular choice

$$n(\vec{r};\alpha) = n_0(\vec{r}) + \alpha[n(\vec{r}) - n_0(\vec{r})] \tag{9}$$

reduces (8) to

$$\beta[v_n(\vec{r}) - v_0(\vec{r})] = -\ln[n(\vec{r})/n_0(\vec{r})] + \int_0^1 d\alpha \int d^3r' C(\vec{r},\vec{r}\,';\alpha) \times [n(\vec{r}\,') - n_0(\vec{r}\,')] . \tag{10}$$

It is important to point out that the existence of the functional $\tilde{\Omega}[n]$ guarantees that the result (10) is independent of the path of integration.[6,7] Further simplification will result if we choose the reference state to be one of uniform density with

$$n_0(\vec{r}) = n_0 = \text{const}$$

$$\text{and} \tag{11}$$

$$v_0(\vec{r}) = 0 .$$

Then (10) becomes

$$\beta v_n(\vec{r}) = -\ln\left(\frac{n(\vec{r})}{n_0}\right) + \int_0^1 d\alpha \int d^3r' \, C(\vec{r},\vec{r}\,';\alpha) \times [n(\vec{r}\,') - n_0] . \tag{12}$$

A further integration of (12) using (2) and the same path yields

$$\beta(\Omega - \Omega_0) = \beta \int d^3r \, v(\vec{r})[n(\vec{r}) - n_0] + \int d^3r \, n(\vec{r}) \ln\left(\frac{n(\vec{r})}{n_0}\right) - \int d^3r [n(\vec{r}) - n_0] - \int_0^1 d\alpha \int_0^\alpha d\alpha' \int d^3r \, d^3r' \, C(\vec{r},\vec{r}\,';\alpha')[n(\vec{r}) - n_0][n(\vec{r}\,') - n_0] ; \tag{13}$$

Ω_0 is the grand free energy of the reference state.

The theorem of Mermin guarantees that Ω is unique; i.e., the free energy calculated using (13) will not depend on the path employed for the functional integrations. Also, assuming that one can calculate $C(\vec{r},\vec{r}\,';\alpha)$ for any density along the path, (13) provides a useful way of finding approximations for Ω and $n(\vec{r})$ given an external potential. The final density can be parametrized and the right-hand side of (13) minimized with respect to the parameters. This procedure is much simpler than finding the exact density by solving the integral equation that results from combining (12) and (2).

Next, we compare (13) with the approximate theory developed in Ref. 1. This comparison is facilitated by making the definitions

$$\tilde{C}(\vec{r},\vec{r}\,') \equiv 2 \int_0^1 d\alpha \int_0^\alpha d\alpha' \, C(\vec{r},\vec{r}\,';\alpha') \tag{14}$$

and

$$\tilde{C}_0(\vec{r}) \equiv \int d^3r' \, \tilde{C}(\vec{r},\vec{r}\,') . \tag{15}$$

Given (14) and (15), we may write (13) as

$$\Omega - \Omega_0 = \int d^3r \, \omega(\vec{r}) + \int d^3r \, v(\vec{r})[n(\vec{r}) - n_0] + \frac{k_B T}{4} \int d^3r \, d^3r' \, \tilde{C}(\vec{r},\vec{r}\,')[n(\vec{r}) - n(\vec{r}\,')]^2 , \tag{16}$$

where

$$\omega(\vec{r}) = k_B T \left[n(\vec{r}) \ln\left(\frac{n(\vec{r})}{n_0}\right) - [n(\vec{r}) - n_0] - \tilde{C}_0(\vec{r}) \frac{[n(\vec{r}) - n_0]^2}{2} \right] . \tag{17}$$

In deriving (16) the symmetry relation $C(\vec{r},\vec{r}\,') = C(\vec{r}\,',\vec{r})$, which follows from the fact that $C(\vec{r},\vec{r}\,')$ is a second variational cross derivative of $\tilde{\Omega}$, has been used. The approximate theory of Ref. 1 is stated by an equation strikingly similar to (16):

$$\Omega_a = \int d^3r \, \omega_a(\vec{r}) + \int d^3r \, v(\vec{r}) n(\vec{r}) + \frac{k_B T}{4} \int d^3r \, d^3r' \, C_a(\vec{r} - \vec{r}\,';\bar{n})[n(\vec{r}) - n(\vec{r}\,')]^2 . \tag{18}$$

In this expression, $\omega_a(\vec{r})$ is the free energy density of a *uniform* system with density $n(\vec{r})$ and $C_a(\vec{r} - \vec{r}\,';\bar{n})$ is the direct correlation function of a uniform system at density $\bar{n}$. The density $\bar{n}$ is chosen in a convenient and physically reasonable manner, the usual choice being

$$\bar{n} = [n(\vec{r}) + n(\vec{r}\,')]/2 . \tag{19}$$

Equation (18) is a guess, motivated by the idea that the free energy in a nonuniform system should be given approximately by a local term $\omega_a(\vec{r})$ plus a nonlocal term arising from the nonuniformity and having the appearance of an effective interaction between different parts of the system. The kernel $C_a(\vec{r}-\vec{r}';\bar{n})$ for the nonlocal term was shown to be the direct correlation function in the weakly nonuniform case by invoking linear-response theory. In this limit, $\bar{n}$ is the average density of the system and (18) is an expansion of Ω through second order in density differences. Given large density variations, $\bar{n}$ accounts in an approximate fashion for terms higher than second order in the expansion. This procedure is clearly open to question beyond the regime where linear-response theory is valid.

It seems likely that one of the reasons why the theory of Ref. 1 gives such reasonable results is the similarity of (16) and (18). Also, one can show that, for the case of a uniform final density $n(\vec{r})=n$, $\omega(\vec{r})$ is just the difference in the Helmholtz free energy densities $f(n)$ and $f(n_0)$, thus further exposing the similarity. A proof of the preceding assertion follows from integrating the uniform system relations[4]

$$\left(\frac{\partial P}{\partial n}\right)_T=\beta^{-1}[1-nC_0(n,T)] \qquad (20)$$

and

$$\left(\frac{\partial \mu}{\partial n}\right)_T=\frac{\beta^{-1}}{n}[1-nC_0(n,T)] \qquad (21)$$

between n_0 and n, changing the integration variable to α, and using the fact that $f(n)=-P(n)+n\mu(n)$. Here, $C_0(n,T)$ is the $\vec{q}=0$ Fourier component of the direct correlation function. Finally, note that $\omega(n)=f(n)-\mu n$ and that the integral over $v(\vec{r})$ in (16) accounts for changes in μ that occur when going from the initial to final uniform densities. In fact, the procedure just outlined was employed[1] to obtain ω_a from C_a for use in (18). We conclude that the form of (18) is correct and that the theory presented in Ref. 1 amounts to guessing the average correlation functions defined in (14) and (15).

The use of (10) obviates the need for employing either the density-difference expansion or a somewhat arbitrary choice of the average density $\bar{n}$. The lone remaining question is how to obtain $C(\vec{r},\vec{r}')$ given a nonuniform density $n(\vec{r})$. In our previous work,[1] C_a was obtained from the Percus-Yevick equation[8] for a uniform system. The same may be done here, generalizing to the case of nonuniformity. The Percus-Yevick equation is

$$C(\vec{r},\vec{r}')=[1+h(\vec{r},\vec{r}')][1-e^{\beta V(\vec{r}-\vec{r}')}], \qquad (22)$$

where $V(\vec{r})$ is the interparticle pair potential. The coupled equations (7) and (22) must be solved for density distributions which occur in the parameter path integrations in order to make any applications of (16). In the general case, this operation would involve a massive amount of numerical work. However, in the course of the work presented in Ref. 1 we developed numerical techniques which permit the solution of (7) and (22) for a uniform system in a few seconds using an IBM 370/168. We are confident that these techniques can be extended to handle nonuniform systems.[9] Should this confidence not be misplaced, the theory of equilibrium nonuniform classical fluids will have advanced to a position roughly equivalent to that of the theory of uniform systems in which no approximations beyond those used in deriving results such as the Percus-Yevick or hypernetted chain equations[4] need be invoked.

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[1] C. Ebner, W. F. Saam, and D. Stroud, Phys. Rev. A 14, 2264 (1976).

[2] Density-functional theories used in other areas of physics contain similar questionable approximations. See the review article by N. D. Lang, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1973), Vol. 28, p. 255. C. Ebner and W. F. Saam [Phys. Rev. B 12, 923 (1975)] used a theory similar to that of Ref. 1 for superfluid He^4 at $T=0$. Further references may also be found in this paper.

[3] N. D. Mermin, Phys. Rev. 137, A1441 (1965).

[4] See e.g., R. Balescu, *Equilibrium and Non-Equilibrium Statistical Mechanics* (Wiley, New York, 1975), Chap. 7. See also Ref. 5.

[5] J. L. Lebowitz and J. K. Percus, J. Math. Phys. 4, 116 (1963). Functional techniques for classical systems were first developed in this paper. However, applications were essentially limited to systems whose properties vary slowly with position.

[6] This essential point was apparently not recognized by the authors of Ref. 5.

[7] Evidently a reasonable degree of mathematical regularity is assumed here. Consequently our results may not apply to the critical region of a continuous (i.e., second-order) phase transition.

[8] J. K. Percus and G. J. Yevick, Phys. Rev. 110, 1 (1958). In this work only uniform systems were considered. See Ref. 5 for the nonuniform case.

[9] A practical technique for solving (7) and (22) in one and three dimensions for a wide range of nonuniform densities which vary in one dimension only has already been developed. C. Punyanitya, private communication.