

Comments

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Comment on “Modified weighted-density-functional theory of nonuniform classical liquids”

Soon-Chul Kim and Gerald L. Jones

Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556

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We investigate some properties of a recently proposed [Denton and Ashcroft, Phys. Rev. A **39**, 4701 (1989)] modification of the weighted-density approximation and compare them with properties of the traditional version. We show that this approximation leads to the hypernetted-chain equation of state for homogeneous systems.

In a recent paper<sup>1</sup> Denton and Ashcroft have introduced a modified weighted-density approximation (MWDA) in which the excess free energy depends on a global average of the density rather than the local average.<sup>2</sup> They applied this method to the freezing problem for hard spheres and obtained good results compared with the molecular-dynamics data. This formulation has both desirable and undesirable properties. In the following we discuss these properties and show that this approximation implies the hypernetted-chain (HNC) equation of state for the homogeneous system.

The MWDA theory is defined by the assumption that the excess free energy per particle is simply a function of a global average of the local density. That is, that

$$F_{ex}[\rho]/N = f(\hat{\rho}), \tag{1}$$

where

$$\hat{\rho} = \frac{1}{N} \int d\mathbf{r}_1 \rho(\mathbf{r}_1) \int d\mathbf{r}_2 \rho(\mathbf{r}_2) \bar{w}(\mathbf{r}_1 - \mathbf{r}_2, \hat{\rho}), \tag{2}$$

$\bar{w}$  is a normalized weighting function, and  $N$  is the number of particles in the system.

The introduction of this assumption is very useful, because from the second functional derivative of excess free energy with respect to density  $\rho(\mathbf{r})$  one obtains a simple analytic relationship between the weighting function  $\bar{w}(r, \rho)$  and the two-particle direct correlation function  $c^{(2)}(r, \rho)$  for the homogeneous system:

$$\bar{w}(r, \rho) = -\frac{1}{2f'(\rho)} \left[ \beta^{-1} c^{(2)}(r, \rho) + \frac{1}{V} \rho f''(\rho) \right]. \tag{3}$$

The simplicity of this relationship compared to the corresponding relationship in the usual weighted density

theory is the main advantage of the MWDA. On the other hand, there is an undesirable property. One can show that the  $n$ -particle direct correlation functions for  $n \geq 3$  vanish, because the functional derivatives of the weighted density  $\hat{\rho}$  with respect to  $\rho(\mathbf{r})$  for the homogeneous system vanish in the thermodynamic limit. This is clear from the form of (2).

To derive the HNC equation from the MWDA for the homogeneous system, we follow a method<sup>3</sup> that we have used for the usual weighted-density theory. The problem is to relate the functions  $f$  and  $\bar{w}$  of the MWDA to the intermolecular potential  $\phi(r)$ . To do this, we use an identity given by Percus.<sup>4</sup> The idea is that the pair distribution function  $g(\mathbf{r}, \mu)$  of a system at chemical potential  $\mu$  and zero external potential is simply related to the local density  $\rho(\mathbf{r}, \mu)$  of the same system with an external potential  $u(\mathbf{r})$  provided by a fixed particle at the origin interacting with the system particles by intermolecular potential  $\phi(\mathbf{r})$ . In particular,

$$\rho(\mu)_0 g(\mathbf{r}, \mu)_0 = \rho(\mathbf{r}, \mu)_{\phi(\mathbf{r})}. \tag{4}$$

In the density-functional theory the equilibrium density in the presence of an external potential  $u(\mathbf{r})$  is determined by the extremal condition,

$$c^{(1)}(\mathbf{r}; [\rho]) \equiv -\beta \frac{\delta F_{ex}[\rho]}{\delta \rho(\mathbf{r})} = -\beta \mu + 3\beta \ln \Lambda + \ln \rho(\mathbf{r}) + \beta u(\mathbf{r}), \tag{5}$$

where  $\Lambda$  is the thermal de Broglie wavelength. A straightforward computation from (1) and (2) shows that in the MWDA

$$c^{(1)}(\mathbf{r}; [\rho]) = -\beta f(\hat{\rho}) + \beta f'(\hat{\rho}) \left[ \frac{1}{N} \int d\mathbf{t} \rho(\mathbf{t}) \int d\mathbf{s} \rho(\mathbf{s}) \bar{w}(\mathbf{t} - \mathbf{s}, \hat{\rho}) - 2 \int d\mathbf{s} \rho(\mathbf{s}) \bar{w}(\mathbf{r} - \mathbf{s}, \hat{\rho}) \right] \times \left[ 1 - \frac{1}{N} \int d\mathbf{s} \rho(\mathbf{s}) \int d\mathbf{t} \rho(\mathbf{t}) \bar{w}'(\mathbf{s} - \mathbf{t}, \hat{\rho}) \right]^{-1}, \tag{6}$$

where the notation  $[\rho]$  is to emphasize that  $c^{(1)}$  is to be regarded as a functional of the single-particle density  $\rho(\mathbf{r})$  and  $\bar{w}'$  is the derivative of  $\bar{w}$  with respect to the second ( $\hat{\rho}$ ) argument. We apply the equilibrium condition (5) to the uniform state ( $\mu, u(\mathbf{r})=0, V$ ) of the density  $\rho$  and the nonuniform state ( $\mu, u(\mathbf{r})=\phi(\mathbf{r}), V$ ) whose density is given by the Percus condition (4), and eliminate  $\mu$  between the two equations to obtain

$$c^{(1)}(\rho) = c^{(1)}(\mathbf{r}; [\rho g]) - \ln g(r) - \beta \phi(r). \quad (7)$$

For the uniform case  $\hat{\rho}=\rho$ , and (6), with the normalization of  $\bar{w}$ , gives

$$c^{(1)}(\rho) = -\beta [f(\rho) + \rho f'(\rho)]. \quad (8)$$

Now consider the nonuniform case where the density is given by the Percus condition (4). Let  $\hat{\rho}'$  be the corresponding global average from (2). Using (3) and (4) in (6) gives, after some manipulation,

$$c^{(1)}(\mathbf{r}; [\rho g]) = -\beta \left[ f(\hat{\rho}') + \rho f'(\hat{\rho}') + 2\rho f'(\hat{\rho}') \int \bar{w}(\mathbf{r}-\mathbf{s}, \hat{\rho}') [g(s) - 1] d\mathbf{s} \right] + O(1/N), \quad (9)$$

where  $O(1/N)$  indicates several terms which will vanish in the thermodynamic limit. It is very easy to show from (2) that  $\hat{\rho}' = \rho + O(1/N)$  so that when the thermodynamic limit of (9) is taken, and (3) is used, we have

$$c^{(1)}(\mathbf{r}; [\rho g]) = -\beta [f(\rho) + \rho f'(\rho)] + \rho \int c^{(2)}(\mathbf{r}-\mathbf{s}, \rho) [g(s) - 1] d\mathbf{s}. \quad (10)$$

With (8) and (10), (7) yields

$$\ln g(r) = -\beta \phi(r) + \rho \int c^{(2)}(\mathbf{r}-\mathbf{s}, \rho) [g(s) - 1] d\mathbf{s}. \quad (11)$$

The Ornstein-Zernike relationship with (11) is just the usual HNC equation. The HNC equation is known not to give an accurate equation of state for strong repulsive potentials,<sup>5</sup> whereas we have shown<sup>3</sup> that, at least at low densities, the usual weighted-density approximation theory is quite accurate. In this respect the traditional weighted-density theory may be preferable even though the MWDA theory is computationally simpler.

<sup>1</sup>A. R. Denton and N. W. Ashcroft, Phys. Rev. A **39**, 4701 (1989).

<sup>2</sup>P. Tarazona, Phys. Rev. A **31**, 2672 (1985); W. A. Curtin and N. W. Ashcroft, Phys. Rev. A **32**, 2909 (1985).

<sup>3</sup>G. I. Jones and S. C. Kim, J. Stat. Phys. **56**, 709 (1989).

<sup>4</sup>J. K. Percus, in *The Equilibrium Theory of Classical Fluids*,

edited by H. L. Frisch and J. L. Lebowitz (Benjamin, New York, 1964).

<sup>5</sup>J. A. Barker and D. Henderson, Rev. Mod. Phys. **48**, 587 (1976); F. H. Ree, R. N. Keeler, and S. L. MacCarty, J. Chem. Phys. **44**, 3407 (1966).