

Thermodynamic consistency between the energy and virial routes in the mean spherical approximation for soft potentials

Andrés Santos^{a)}

Departamento de Física, Universidad de Extremadura, E-06071 Badajoz, Spain

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Standard statistical-mechanical formulas relate the thermodynamic properties of a fluid to the two-body interaction potential $\varphi(r)$ and the associated radial distribution function $g(r; \rho, \beta)$,¹ where ρ is the number density and $\beta=1/k_B T$ is the inverse temperature. When an approximation is used to get $g(r; \rho, \beta)$, there is in general no guarantee that those different formulas or routes are thermodynamically self-consistent. In fact, some liquid state theories contain one or more adjustable state-dependent parameters which are tuned to achieve thermodynamic consistency between two or more routes. This is the case, for instance, of the modified hypernetted-chain closure,² the Rogers-Young closure,³ the Zerah-Hansen closure,⁴ the self-consistent Ornstein-Zernike approximation,⁵ the hierarchical reference theory,⁶ Lee's theory based on the zero-separation theorems,⁷ the generalized mean spherical approximation,⁸ or the rational-function approximation.⁹ It is then remarkable when an approximate theory for $g(r; \rho, \beta)$ satisfies a condition of thermodynamic consistency without being forced to do so. In this context, it is perhaps not sufficiently well-known that the hypernetted-chain (HNC) integral equation provides thermodynamically consistent results through the virial and energy routes, regardless of the potential $\varphi(r)$.¹⁰ More recently, Mladek *et al.*¹¹ have shown that the mean spherical approximation (MSA) is exactly solvable for the Gaussian core model and have found that the virial and energy routes to thermodynamics are equivalent in that case as well.

The aim of this note is to place Mladek *et al.* finding¹¹ in a broader context by proving the thermodynamic consistency between the virial and energy routes for (a) any "soft" potential and (b) within a class of approximations that includes the MSA as a particular case.

The virial and energy routes to thermodynamics read¹

$$\frac{\beta p}{\rho} \equiv Z(\rho, \beta) = 1 - \frac{1}{2d} \rho \beta \int \mathbf{dr} g(r; \rho, \beta) \mathbf{r} \cdot \nabla \varphi(r), \quad (1)$$

$$u(\rho, \beta) = \frac{d}{2\beta} + \frac{1}{2} \rho \int \mathbf{dr} g(r; \rho, \beta) \varphi(r), \quad (2)$$

respectively, where p is the pressure, Z is the compressibility factor, d is the dimensionality of the system, and u is the internal energy per particle. The condition of thermodynamic consistency between both routes is

$$\rho \frac{\partial}{\partial \rho} u(\rho, \beta) = \frac{\partial}{\partial \beta} Z(\rho, \beta). \quad (3)$$

Let us now consider an interaction potential verifying the boundary conditions

$$\lim_{r \rightarrow 0} r^d \varphi(r) = 0, \quad \lim_{r \rightarrow \infty} r^d \varphi(r) = 0. \quad (4)$$

While the second condition means that the potential is sufficiently short ranged, the first condition defines the kind of soft potentials to be considered here. It includes bounded potentials (such as the Gaussian core model¹² or the penetrable sphere model¹³), logarithmically diverging potentials,¹⁴ or even potentials diverging algebraically as $\varphi(r) \sim r^{-n}$ with $n < d$. On the other hand, conventional molecular models (such as hard spheres, square-well fluids, and Lennard-Jones fluids) are excluded from the class of potentials (4). Equation (4) implies that $\tilde{\varphi}(0)$ is finite, where the Fourier transform of the potential is

$$\tilde{\varphi}(k) = \mathcal{F}[\varphi(r)] = \int \mathbf{dr} e^{-i\mathbf{k} \cdot \mathbf{r}} \varphi(r). \quad (5)$$

Introducing the total correlation function $h(r; \rho, \beta) \equiv g(r; \rho, \beta) - 1$, Eqs. (1) and (2) can be rewritten as

$$Z(\rho, \beta) = 1 + \frac{1}{2} \rho \beta \tilde{\varphi}(0) - \frac{1}{2d} \rho \beta I_v(\rho, \beta), \quad (6)$$

$$u(\rho, \beta) = \frac{d}{2\beta} + \frac{1}{2} \rho \tilde{\varphi}(0) + \frac{1}{2} \rho I_e(\rho, \beta), \quad (7)$$

where

$$\begin{aligned} I_v(\rho, \beta) &\equiv \int \mathbf{dr} h(r; \rho, \beta) \mathbf{r} \cdot \nabla \varphi(r) \\ &= - \frac{1}{(2\pi)^d} \int \mathbf{dk} \tilde{h}(k; \rho, \beta) \frac{\partial}{\partial \mathbf{k}} \cdot [\mathbf{k} \tilde{\varphi}(k)], \end{aligned} \quad (8)$$

$$\begin{aligned} I_e(\rho, \beta) &\equiv \int \mathbf{dr} h(r; \rho, \beta) \varphi(r) \\ &= \frac{1}{(2\pi)^d} \int \mathbf{dk} \tilde{h}(k; \rho, \beta) \tilde{\varphi}(k). \end{aligned} \quad (9)$$

In the last equalities of Eqs. (8) and (9), $\tilde{h}(k; \rho, \beta) \equiv \mathcal{F}[h(r; \rho, \beta)]$ and standard steps have been followed. The consistency condition (3) becomes

$$\Delta(\rho, \beta) \equiv \frac{\partial}{\partial \rho} [\rho I_e(\rho, \beta)] + \frac{1}{d} \frac{\partial}{\partial \beta} [\beta I_v(\rho, \beta)] = 0. \quad (10)$$

Equation (10) is of course satisfied if the *exact* $\tilde{h}(k; \rho, \beta)$ is used to evaluate $I_v(\rho, \beta)$ and $I_e(\rho, \beta)$. On the other hand, as proven below, the same happens with any *approximate* function $\tilde{h}(k; \rho, \beta)$ which, when **divided** by ρ , depends on ρ , β , and k through the scaled variable $z \equiv \rho \beta \tilde{\varphi}(k)$ only, i.e.,

$$\tilde{h}(k; \rho, \beta) = \rho^{-1} F(z), \quad z \equiv \rho \beta \tilde{\varphi}(k), \quad (11)$$

where the function $F(z)$ does not need to be specified. The scaling form (11) implies

$$\frac{\partial}{\partial \beta} [\rho \tilde{h}(k; \rho, \beta)] = \tilde{h}(k; \rho, \beta) + \frac{\partial}{\partial \rho} [\rho \tilde{h}(k; \rho, \beta)], \quad (12)$$

$$\frac{\partial}{\partial \rho} [\rho \tilde{h}(k; \rho, \beta)] \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{k}} \tilde{\varphi}(k) = \tilde{\varphi}(k) \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{k}} \tilde{h}(k; \rho, \beta). \quad (13)$$

Applying Eq. (12) in the definition of $\Delta(\rho, \beta)$, Eq. (10), one gets

$$\Delta(\rho, \beta) = -\frac{1}{d(2\pi)^d} \int d\mathbf{k} \left\{ \tilde{h}(k; \rho, \beta) \frac{\partial}{\partial \mathbf{k}} \cdot [\mathbf{k} \tilde{\varphi}(k)] + \frac{\partial}{\partial \rho} [\rho \tilde{h}(k; \rho, \beta)] \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{k}} \tilde{\varphi}(k) \right\}. \quad (14)$$

Finally, use of Eq. (13) yields $\Delta(\rho, \beta) = 0$, which proves the thermodynamic consistency between Eqs. (1) and (2) within the class of approximations (11). Furthermore, Z and u adopt the forms

$$Z(\rho, \beta) = 1 + \frac{1}{2} \tilde{\varphi}(0) \alpha - \beta \zeta_v(\alpha), \quad (15)$$

$$\beta u(\rho, \beta) = \frac{d}{2} + \frac{1}{2} \tilde{\varphi}(0) \alpha - \beta \zeta_e(\alpha), \quad (16)$$

where $\alpha \equiv \rho \beta$, $\zeta_v(\alpha) \equiv \rho I_v(\rho, \beta) / 2d$, and $\zeta_e(\alpha) \equiv -\rho I_e(\rho, \beta) / 2$. Equation (10) implies the relation $\alpha \zeta'_e(\alpha) = d[\alpha \zeta'_v(\alpha)] / d\alpha$, where $\zeta'_e(\alpha) \equiv d\zeta_e(\alpha) / d\alpha$.

It must be noted that the compressibility route is inconsistent with the virial and energy routes, i.e., $[1 + \rho \tilde{h}(0; \rho, \beta)]^{-1} \neq \partial(\rho Z) / \partial \rho$, for approximations of the form (11). While the (reduced) isothermal compressibility $1 + \rho \tilde{h}(0; \rho, \beta) = 1 + F(\tilde{\varphi}(0) \alpha)$ depends on ρ and β through the product $\alpha = \rho \beta$ only, Eq. (15) yields $\partial(\rho Z) / \partial \rho = 1 + \tilde{\varphi}(0) \alpha - \beta \alpha \zeta'_e(\alpha)$, the last term depending on both α and β .

The MSA for soft potentials¹¹ consists of assuming the random-phase approximation $c(r; \rho, \beta) = -\beta \varphi(r)$ for the direct correlation function at any distance. The Ornstein-Zernike relation¹ then gives Eq. (11) with $F(z) = -z / (1 + z)$,

so that this version of the MSA is thermodynamically consistent through the virial and energy routes. However, they are inconsistent with the compressibility route: $[1 + \rho \tilde{h}(0; \rho, \beta)]^{-1} - \partial(\rho Z) / \partial \rho = \beta \alpha \zeta'_e(\alpha)$.

The work presented here and elsewhere¹⁵ might have a didactic value in showing that relatively simple mathematics allows one to check the thermodynamic self-consistency between the virial and energy routes in some important special cases.

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- ^{a)}URL: <http://www.unex.es/fisteor/andres/>. Electronic mail: andres@unex.es
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