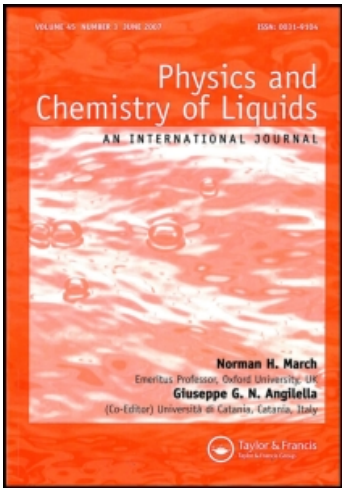

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Entropy and Pressure of a Liquid with an Inverse Power Potential Reference System

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Letter

Entropy and Pressure of a Liquid with an Inverse Power Potential Reference System

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The Gibbs–Bogoliubov variational method is applied to a simple liquid using an inverse power potential reference system; simple expressions are derived for the entropy and pressure. It is argued that such inverse power systems are worthy of study by computer simulation, at the same depth as has hitherto been reserved for the hard sphere and coulombic limiting cases, with the above variational application in mind.

Liquids with atoms interacting via inverse power potentials of the type $(\sigma/r)^p$ have been much studied by computer simulation and have played an important role in elucidating the thermodynamic and structural properties of real systems. Most notable is the hard sphere case $p = \infty$ which has been at the forefront of such endeavours for the past decade[1,2] but the opposite coulombic limit $p = 1$ has also been thoroughly investigated[3] and various applications made (for example, by Evans and Sluckin to liquid alkalis[4] and by Grimson to colloids[5]). The intermediate cases $n = 4, 6, 9, 12$ have also been studied by computer simulation (see, e.g., Hansen and Schiff[6]) and found application in the alkalis by Schiff[7] and Yokoyama and Ono.[8]

Such simple systems contain only a single coupling constant $\Gamma = (\sigma/a)^p/k_B T$ and so are suitable for detailed solution and economic tabulation over all relevant values of the parameters. In this expression for Γ, a is the measure of the inter-particle separation obtained from the particle number density n by $a = (3n/4\pi)^{1/3}$. One may write the Helmholtz free energy (per ion) as

$$F_0 = \tfrac{3}{2}k_B T + V_0 - TS_0 \tag{1}$$

where V_0 is the potential energy and S_0 is the entropy. The latter may, for

subsequent convenience, be written

$$S_0 = S_{id} + \Delta S_0 \tag{2}$$

where S_{id} is an ideal gas contribution.

An important way of relating such a 'reference' system as the above to a 'real' system of the same density and atomic mass, but with different interaction

$$V = \sum_{i<j} v(r_{ij}), \tag{3}$$

is to use the Gibbs–Bogoliubov variational method. This states that a free energy estimate for the real system may be found from

$$F = F_0 + \langle V \rangle_0 - V_0 \tag{4}$$

where $\langle V \rangle_0$ is the expectation of V averaged over the reference system. Explicitly, we have

$$\langle V \rangle_0 = \tfrac{1}{2} n \int v(r) g_0\left(\frac{r}{a}, \Gamma\right) \mathrm{d}\mathbf{r} \tag{5}$$

where $g_0(r/a, \Gamma)$ is the reference system's radial distribution function, the parameter dependence of which is shown explicitly. In (4), a choice of Γ must be made; this is done by using the variational condition

$$\left(\frac{\partial F}{\partial \Gamma}\right)_{n,T} = 0. \tag{6}$$

Using (1) and (2), we may rewrite (4) as

$$F = F_{id} - T\Delta S_0 + \langle V \rangle_0 \tag{7}$$

where F_{id} is an ideal gas contribution and ΔS_0 (defined by (2)) depends only on Γ (and not on σ, a, T separately). Furthermore, as is clear from (5), $\langle V \rangle_0$ is a function of n and Γ only (taking $v(r)$ independent of T).

Under these circumstances, the entropy estimate for the real system is obtained as follows:

$$S = -\left(\frac{\partial F}{\partial T}\right)_n = -\left(\frac{\partial F}{\partial T}\right)_{n,\Gamma} - \left(\frac{\partial F}{\partial \Gamma}\right)_{n,T}\left(\frac{\partial \Gamma}{\partial T}\right)_n. \tag{8}$$

The final contribution vanishes by the variational condition (6), while the insertion of (7) into the other term gives

$$\begin{aligned} S &= -\left\{\frac{\partial}{\partial T}(F_{id} - T\Delta S_0 + \langle V \rangle_0)\right\}_{n,\Gamma} \\ &= S_{id} + \Delta S_0 + 0 = S_0 \end{aligned} \tag{9}$$

by (2). That is, the entropy of the real system is given by the expression for the reference system with the optimum Γ, given by (6), inserted.

A rather simple expression can also be obtained for the pressure. We have

$$\frac{P}{n^2} = \left(\frac{\partial F}{\partial n}\right)_T = \left(\frac{\partial F}{\partial n}\right)_{T,\Gamma} + \left(\frac{\partial F}{\partial \Gamma}\right)_{n,T}\left(\frac{\partial \Gamma}{\partial n}\right)_T \tag{10}$$

The final contribution vanishes because of (6), while the insertion of (7) into the other term gives

$$\begin{aligned} P &= n^2\left\{\frac{\partial}{\partial n}(F_{\mathrm{id}} - T\Delta S_0 + \langle V\rangle_0)\right\}_{T,\Gamma} \\ &= nk_BT + 0 + n^2\left\{\frac{\partial}{\partial n}\frac{1}{2}\int v(r)g_0\left(\frac{r}{a},\Gamma\right)d(n\mathbf{r})\right\}_{T,\Gamma} \end{aligned} \tag{11}$$

This last term follows from using (5) and simplifies by first changing the variables to $\mathbf{r}/a$, then performing the differentiation (on v only) and finally returning to the original variables. This leads to

$$P = nk_BT - \tfrac{1}{6}n^2\int v(r)\left(r\frac{\partial v}{\partial r} - 3n\frac{\partial v}{\partial n}\right)g_0\left(\frac{r}{a},\Gamma\right)\mathrm{d}\mathbf{r} \tag{12}$$

This is the exact[9] equation of state for the system described by the (possibly density-dependent) interaction (3) but modified in that the exact radial distribution has been replaced by the reference one.

Special cases of the above results for the entropy and pressure have already been published. Edwards and Jarzynski[10] obtained (9) for hard spheres while Watabe and Young[11] proved (12) for the same reference system. Both results were established by Young[12] for the coulombic (one-component plasma) case.

The results obtained here can be generalized somewhat. First a term $U(n)$, which is independent of the atomic configuration, can be added to (3). The subsequent algebra is modified in a rather trivial way and the result (9) is preserved unchanged. Equation (12), however, is modified by the addition of a term $n^2U'(n)$ to the right side. The recognition that such a term is present is vital to a proper description of the thermodynamic properties of metals.[1]

A second possible generalization is to systems where the interatomic potential of the reference system is given by a linear combination of inverse powers of the type $(\sigma_i/r)^{p_i}$. This includes the Lennard-Jones case and similar types. Then there are a family of parameters $\{\Gamma_i\}$ instead of the single Γ used previously. This requires simple, obvious changes in the algebra and the results (9) and (12) follow once more. Unfortunately, the addition parameters

involved are likely to prove a severe obstacle to the systematic, economic but yet detailed description of such systems by computer simulation.

On the other hand, as has been demonstrated in the two limits, the use of a single inverse power potential is entirely practicable. Furthermore, in view of the high quality of fittings to observed structure factors[7,8] which have already been achieved using the partial information at present available, the prospects are very good for the successful application of such systems for reference purposes within a Gibbs–Bogoliubov context.

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