UPPER BOUNDS ON THE FREE ENERGY

OF A LENNARD-JONES SYSTEM

by

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ABSTRACT

Expressions are derived that bound from above the Helmholtz free energy of a classical Lennard-Jones system. At any temperature they provide a finite upper bound on the free energy at all finite densities.

The purpose of this note is to call attention to some upper bounds on the Helmholtz free energy of a system with a Lennard-Jones pair potential. The bounds follow from the simple application of a familiar inequality of the sort discussed by Gibbs, Peierls, Bogoliubov, and others[1].

Let f be the Helmholtz free energy per particle, ρ the number density, and $g(\underset{\sim}{r})$ the pair (radial) distribution function of a classical single-species system, the energy of which is a sum of one-body and two-body contributions. If the pair potential $v(\underset{\sim}{r})$ is arbitrarily decomposed into the sum of two terms, $v(\underset{\sim}{r}) = v^{o}(\underset{\sim}{r})+\lambda w(\underset{\sim}{r})$, and a superscript zero is used to denote quantities associated with the system in which $v(\underset{\sim}{r}) = v^{o}(\underset{\sim}{r})$ the basic inequality we shall use can be written as[1]

$$f \leq f^{o} + \tfrac{1}{2}\lambda\rho\int g^{o}(\underset{\sim}{r})\, w(\underset{\sim}{r})\, d\underset{\sim}{r} \; , \qquad (1)$$

Although (1) is widely known, the following observation, which consitutes our point of departure, does not seem to have been systematically exploited: If $v(\underset{\sim}{r}) = 4\varepsilon[(\sigma/r)^{12}-(\sigma/r)^{6}]$ (where $r=|\underset{\sim}{r}|$), $v^{o}(\underset{\sim}{r}) = \infty$ for $r < d$ (where d is an arbitrary length) and 0 elsewhere, and $w = v-v^{o}$, then despite the highly singular nature of $w(\underset{\sim}{r})$ for $r < d$, the integrand appearing in (1) is finite for all r and any $0 < d < \infty$, since for $r < d$, $g^{o}(\underset{\sim}{r})$ "vanishes much more strongly" than $w(\underset{\sim}{r})$ diverges. We can give a two-step argument for the same conclusion that does not involve the product of singular functions by writing $v = v^{<}+\lambda v^{>}$ where $v^{<} = v$ for $r \leqslant d$ and zero elsewhere. Then f^{LJ} (f for v) is less than f for $v^{o}+\lambda v^{>}$ at any given $\beta[= 1/kT]$ and ρ, since we are clearly decreasing the value of the configuration integral by replacing $v^{<}$ by v^{o}. We can then use (1) on f for $v^{o}+\lambda v^{>}$ with $w = v^{>}$. Thus we arrive at the inequality

$$f^{LJ} \leq f^{o} + \tfrac{1}{2}\lambda\rho\int g^{o}(\underset{\sim}{r})\, v^{>}(\underset{\sim}{r})\, d\underset{\sim}{r} \; . \qquad (2)$$

Expression (2) can be used in two ways. Firstly, to the extent that f^{O} and g^{O} are known quantities, the right-hand side (rhs) of (2) gives an explicit approximation to f^{LJ} that is of first order in λ and is also an upper bound. By choosing d to minimize the rhs of (2), one obtains the least such upper bound and consequently the best such first-order approximation. Numerical assessments of this approximation can be based on either the highly accurate estimates of f^{O} and g^{O} available from Monte Carlo, molecular dynamical, and density-expansion studies, or the somewhat simpler but less accurate Percus-Yevick values of these quantities. We shall report on this first-order theory elsewhere[2].

The remainder of this note is devoted to the second use of Eq. (2)[3], which is to facilitate the derivation of rigorously exact bounds through the use of rigorous bounds on f^{O} and g^{O}. The simplest of such bounds, though not the best, are those obtained from setting $d=\sigma$, so that only lower bounds on g^{O} need be considered. For high densities, near and less than the close-packing density ρ_M of a system of hard spheres of diameter d, a reasonable upper bound for f^{O} is given in D dimensions by[4]

$$\beta f^{o} \leq -\ln\left\{\rho_M^{-1}\left[(\rho_M/\rho)^{1/D}-1\right]^{D}\right\} \quad , \qquad (3)$$

where in writing (3) and elsewhere in this note we take the thermal wavelength $\Lambda = (h^2/2\pi mkT)^{1/2}$ to be unity. For ρ close to ρ_M the lower bound given by $g^{O} > 0$ can be used and the rhs of (3) (with $D=3$) provides a reasonable bound on βf^{LJ} as well as on βf^{O}. The rhs of (3) becomes infinite when $\rho=\rho_M$ however and is therefore useless for βf^{LJ} when $\rho > \rho_M$. For a finite bound at higher densities, one can choose d to be smaller than σ and break up the integral in (2) into a sum of two terms, the first a positive term involving integration over the domain in which $r \leq \sigma$ and the second a negative term involving the domain over which $r > \sigma$. An upper bound on the negative term is zero while the evaluation of an upper bound on the first term necessitates the use of an upper bound on g^o in the interval $d \leqslant r \leqslant \sigma$. An example of a crude but simple upper bound on g^o that can be employed here is given by $g^o \leqslant (z/\rho)^o$, where z is the fugacity[5]. An upper bound on $(z/\rho)^o$ that remains finite for all $\rho < \rho_M$ can in turn be found by means of the following prescription suggested by Penrose[6]: If a chord is drawn tangent to an upper bound of ρf^o at the density ρ' and if the chord crosses a lower bound of ρf^o at a density ρ less than ρ', then the slope of the chord gives an upper bound at ρ on $\mu = d(\rho f)/d\rho$ and hence on $z = \exp \beta\mu$. An upper bound on ρf^o is given by (3); a lower bound can be obtained by integrating Penrose's result[7] $\beta\mu \geqslant \ln\rho - \ln[1-(\rho/\rho_M)]$. From these observations it follows that

$$g^o(\underset{\sim}{r}) \leqslant (z/\rho)^o \leqslant \min_{\rho<\rho'<\rho_M} \left\{ \left(\frac{\rho}{\rho_M} \left[\left(\frac{\rho_M}{\rho'} \right)^{1/D} - 1 \right]^D \right)^{\frac{\rho'}{\rho'-\rho}} \left[1 - \frac{\rho}{\rho_M} \right]^{\frac{\rho_M-\rho}{\rho'-\rho}} \right\}; \quad (4)$$

Denoting the rhs of (3) as $[\beta f^o]^U$ and the rhs of (4) as $[g^o(r)]^U$ we have finally

$$\beta f^{LJ} \leqslant [\beta f^o]^U + \tfrac{1}{2}\beta\rho \int_{d<r<\sigma} [g^o(\underset{\sim}{r})]^U v^\xi(\underset{\sim}{r})\, d\underset{\sim}{r} \quad (5)$$

For all β this is a bound that remains finite for all finite ρ, no matter how large, if d is chosen to minimize the rhs of (5), subject to the restrictions that $d < \sigma$ and $\rho_M > \rho$. [Note that we can guarantee a finite bound for any finite ρ, simply by making d sufficiently small, since this will guarantee that $\rho < \rho_M$. This insures the existence of a d that will minimize the rhs of (5)].

We turn next to the problem of getting a good bound from (2) at low, rather than high, densities. For simplicity we return to $d=\sigma$. For

References

1. See, for example, A. Isihara, J. Phys. A (Proc. Phys. Soc.) 1, 539 (1968) for a discussion of the equality and some of its variants, as well as relevant references.

2. J. Rasaiah and G. Stell (to be published).

very small ρ we can easily find a better lower bound on g^{0} than zero. For example a straightforward application of the Kirkwood-Salsburg equations[8] yields[9], for $r > d$ and $1 \geqslant 2b\rho$,

$$g^{0}(r) \geqslant \frac{1-4b\rho+\Theta(r)\rho}{(1-2b\rho)[1-2b\rho+(17/64)(2b\rho)^{2}(1-2b\rho)^{-1}]}, \tag{6}$$

where $2b = (4\pi/3)d^{3}$ and $\Theta(r) = (\pi/12)(r^{3}-12d^{2}r+16d^{3})$ for $0 \leqslant r \leqslant 2d$ while $\Theta(r) = 0$ for $r \geqslant 2d$.

A correspondingly appropriate bound for f^{0} at low densities comes from the integration of the lower bound[5], $(\rho/z)^{0} \geqslant 1-2b\rho$, when $1 \geqslant 2b\rho$. Use of this bound yields an expression for $\rho < (2b)^{-1}$:

$$\beta f^{0} \leq \ln\rho + (2b\rho)^{-1}(1-2b\rho)\ln(1-2b\rho). \tag{7}$$

If we let $[g^{0}(r)]^{L} = \min[0, \text{rhs of (6)}]$ and $[\beta f^{0}]^{U2} = $ the rhs of (7), then (2) yields, when $d=\sigma$,

$$\beta f^{LT} \leq [\beta f^{0}]^{U2} + \tfrac{1}{2}\lambda\beta\rho\int[g^{0}(\mathbf{r})]^{L} v'(\mathbf{r})\, d\mathbf{r}, \tag{8}$$

which is appropriate for $\rho < (2b)^{-1}$. Taken together, (5) and (8) provide a reasonably good upper bound over all densities, especially if use is made of the fact that the convex envelope of the curves for the two expressions plotted against ρ^{-1} is also an upper bound. Detailed numerical results will appear elsewhere[9].

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