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Upper and lower bounds in the theory of classical fluids*

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We investigate a number of inequalities, rigorous and conjectured, in the theory of classical fluids. We first investigate approximate calculations, based on the Gibbs inequality, of thermodynamic functions for the Lennard-Jones fluid. If the hard sphere fluid is the reference system, such calculations are simplified when one uses a form of the Gibbs inequality which is valid for systems with the same volume, number of particles and entropy. The internal energy of the Lennard-Jones fluid at moderate and high densities is accurately calculated by the simplified procedure. The procedure does not, however, give accurate values for the pressure at high densities. We also investigate inequalities which apply to fluids for which the pair potential is purely repulsive and has a cutoff. One such (nonrigorous) inequality gives a lower bound to the Helmholtz free energy at fixed density and temperature. It therefore complements the Gibbs inequality, and it gives rise to a fairly simple and accurate procedure for calculation of pressure and internal energy.

I. INTRODUCTION

In recent years accurate analytic expressions for the thermodynamic functions and the correlation functions for the classical hard sphere fluid have become available. It has been possible to derive from these expressions corresponding ones for classical fluids with more realistic interactions. Most of these expressions have been derived via perturbation theory¹⁻⁶; some have proven to be quite accurate.^{5,6}

The most accurate of the just mentioned perturbation methods are extensions of Zwanzig's method.¹ It has been pointed out^{7,8} that Zwanzig's series for the Helmholtz free energy A , when truncated at first order, is a rigorous upper bound to A . This result is a consequence of general inequalities^{9,10} known as the Gibbs inequalities. These are readily derivable by a method used by Gibbs¹¹ in his demonstration of the stationary properties of certain averages over phase space. The upper bound property of the truncated Zwanzig series enables one to treat the diameter of the hard spheres which comprise the unperturbed system as a variational parameter. Such a variational calculation was the point of Refs. 7 and 8. The results are fairly accurate.

In the present paper we further investigate the variational procedure proposed in Refs. 7 and 8. We also consider procedures based on other inequalities, both conjectured and rigorous. The principal outcome of these investigations has been the formulation of some relatively simple but still accurate schemes for calculating the thermodynamic properties of classical fluids. The first such scheme is based on a Gibbs inequality which is valid for systems with the same volume V , number of particles N , and entropy S . The scheme is somewhat simpler than the one proposed in Refs. 7 and 8, which is based on a Gibbs inequality for the canonical ensemble. The simplification, however, leads in certain cases to a considerable loss of accuracy.

In the last part of this investigation we consider particles which interact via a pair potential which is zero when the interparticle separation r is greater than

r_0 and which is purely repulsive for r less than r_0 . Such a system is taken to be the unperturbed system in one of the most accurate of the above mentioned perturbation theories.⁶ We consider both canonical and grand canonical ensembles of such systems. The Gibbs inequality for the canonical ensemble gives an upper bound to A . We conjecture that an expression for A originally derived by Anderson, Weeks, and Chandler¹² gives a lower bound to A . At their extrema the rigorous upper bound and the conjectured lower bound are fairly close to one another in the cases investigated. When differentiated, these expressions for A yield approximate expressions for internal energy U and pressure p which are almost as accurate as those obtained by the approximation proposed in Ref. 12. From a computational standpoint the approximations proposed here are somewhat simpler than the one proposed in Ref. 12.

The Gibbs inequality for the grand canonical ensemble gives a lower bound to p at fixed temperature T and activity z . A rigorous upper bound to $p(z, T)$ can be derived provided the pair potential is purely repulsive and has a cutoff. This upper bound is, however, not easily calculated unless T is very low.

II. THE BASIC INEQUALITIES

A. A Review of the Gibbs Inequalities

We begin by discussing the Gibbs inequalities as they apply to the present work. Derivations are straightforward and can be found elsewhere.^{9,10} We consider two classical systems at equilibrium, a reference system and a problem system. We denote properties of the reference system by a subscript 0. In applications which we shall consider, the reference system is the hard sphere fluid. The interactions in the two systems are assumed to be pairwise additive, and the Hamiltonians H and H_0 are assumed to differ only in that the pair potentials $\phi(r)$ and $\phi_0(r)$ differ.

The Gibbs inequalities take on different forms for

different choices of independent thermodynamic variables. If we assume V and N to be the same for both systems, the Gibbs inequality has the form

$$\frac{A}{kT} \leq \frac{A_0}{kT_0} + \frac{\langle H \rangle}{kT} - \frac{\langle H_0 \rangle}{kT_0}, \quad (\text{A})$$

where k is Boltzmann's constant and $\langle \rangle$ denotes an average over the canonical ensemble of reference systems at equilibrium. If both systems have the same V , T , and chemical potential μ , and if $\langle \rangle$ is taken to be an average over a grand canonical ensemble of reference systems, then the Gibbs inequality has the form

$$pV \geq p_0V - \langle H \rangle + \langle H_0 \rangle. \quad (\text{B})$$

For systems of the type which interest us here, Inequality (A) with $T = T_0$ becomes

$$A(N, V, T) \leq A_0(N, V, T) + \frac{1}{2} \int [\phi(r) - \phi_0(r)] n_0^{(2)}(r) d\mathbf{r}_1 d\mathbf{r}_2 \quad (1)$$

where $n_0^{(2)}$ is the two-body density and $r \equiv |\mathbf{r}_1 - \mathbf{r}_2|$. Inequality (1) is the basis of the variational calculations of Refs. 7 and 8. If S is the same for both systems, we obtain from Inequality (A)

$$\Delta U(N, V, S) \leq \frac{1}{2} \int \phi(r) n_0^{(2)}(r) d\mathbf{r}_1 d\mathbf{r}_2 \quad (2)$$

where ΔU is the configurational (nonideal) part of the internal energy. If V , T and z are the same for both systems, then Inequality (B) becomes for systems of interest

$$p(z, T) \geq p_0(z, T) - (2V)^{-1} \int [\phi(r) - \phi_0(r)] n_0^{(2)}(r) d\mathbf{r}_1 d\mathbf{r}_2. \quad (3)$$

We shall consider applications of Inequalities (1) and (2) in Sec. III.

One can appreciate the physical plausibility of these inequalities if one considers the following exact equation¹³:

$$A = A_0 + \frac{1}{2} \int_0^1 d\lambda \int [\phi(r) - \phi_0(r)] n_\lambda^{(2)}(r) d\mathbf{r}_1 d\mathbf{r}_2 \quad (4)$$

where $n_\lambda^{(2)}$ is the two-body density for a system with pair potential $\phi_0(r) + \lambda[\phi(r) - \phi_0(r)]$. Equation (4) can be written

$$A = A_0 + \frac{1}{2} \int [\phi(r) - \phi_0(r)] n_0^{(2)}(r) d\mathbf{r}_1 d\mathbf{r}_2 + \frac{1}{2} \int_0^1 d\lambda \int [\phi(r) - \phi_0(r)] [n_\lambda^{(2)}(r) - n_0^{(2)}(r)] d\mathbf{r}_1 d\mathbf{r}_2. \quad (5)$$

From Inequality (1) we see that the last term in Eq. (5) must be negative or zero. This implies that the transformation of the pair potential from ϕ_0 to ϕ leads, on the average, to a decrease in the correlation of pairs in regions where the potential goes up and to an increase

in this correlation in regions where the potential goes down. One might have anticipated such a result on the basis of physical intuition.

B. Further Inequalities, Conjectured and Rigorous

Equation (5) is a special case of the more general formula¹⁴

$$A = A_0 + \frac{1}{2} \int_0^1 d\lambda \int \frac{\partial \phi_\lambda}{\partial \lambda}(r) n_\lambda^{(2)}(r) d\mathbf{r}_1 d\mathbf{r}_2. \quad (6)$$

Defining $a_\lambda^{(2)}$ as $n_\lambda^{(2)} \exp(\phi_\lambda/kT)$ and performing some elementary manipulations, we cast Eq. (6) in the form

$$\frac{A}{kT} = \frac{A_0}{kT} - \frac{1}{2} \int [e(r) - e_0(r)] a_0^{(2)}(r) d\mathbf{r}_1 d\mathbf{r}_2 - \frac{1}{2} \int_0^1 d\lambda \int \frac{\partial e_\lambda}{\partial \lambda}(r) [a_\lambda^{(2)}(r) - a_0^{(2)}(r)] d\mathbf{r}_1 d\mathbf{r}_2 \quad (7)$$

where $\phi(r) = \phi_1(r)$ and $e(r) = \exp[-\phi(r)/kT]$. We note that the first two terms on the right of Eq. (7) are less than or equal to the terms on the right of Inequality (1). The last term on the right of Eq. (7) can have either sign. However, one might guess it to be positive provided ϕ and ϕ_0 are purely repulsive potentials with cutoffs.

To justify this last statement (nonrigorously), we consider the potential of average force, call it $W(r) + \phi(r)$, for this system. We have by definition

$$W(r) = -kT \ln[a^{(2)}(r)/n^2],$$

where n is the number density N/V . One interprets $W(r)$ as the contribution to the potential of average force which arises from molecules in the vicinity of a given pair. For potentials of the type just described one might expect $W(r)$ for $r < r_0$ to give rise to a force which pushes the molecules of the pair closer together. Furthermore, one might expect W for $r < r_0$ to decrease on the average as the pair potential increases and to increase on the average as the pair potential decreases. This conjecture implies that on the average $\partial e_\lambda(r)/\partial \lambda$ is opposite in sign to $a_\lambda^{(2)}(r) - a_0^{(2)}(r)$ for that range of r in which the integrand in the last term of Eq. (7) is finite. The last term in Eq. (7) is then positive. Hence, the first two terms on the right of Eq. (7) may constitute a lower bound to A/kT provided ϕ_λ is a purely repulsive potential with a cutoff.

Letting $g(r) = n^{(2)}(r)/n^2$, $y(r) = a^{(2)}(r)/n^2$, and ϕ_0 be the pair potential for hard spheres of diameter d , our conjectured inequality becomes

$$\frac{A}{NkT} \geq \frac{A_0}{NkT} - 2\pi n \left(\int_0^d y_0(r) e(r) r^2 dr + \int_d^{r_0} g_0(r) f(r) r^2 dr \right), \quad (8)$$

where $f(r)$ is the Mayer function, $e(r) - 1$. On the right

of Inequality (8) we see the leading terms of an expansion recently derived by Anderson, Weeks, and Chandler.¹² These authors argued that in the case of a purely repulsive ϕ , this expression is accurate provided ϕ is chosen so that the bracketed terms cancel. If one regards (8) as an inequality, one thinks to treat d as a variational parameter. As will be seen in subsequent sections of this paper, the values of d selected by these two procedures are quite close in those cases for which calculations have been done.

We emphasize that Inequality (8) is a conjecture. The computations reported in Sec. III provide a test, although not a very stringent one, of its validity. In the Appendix we show rigorously that it is valid asymptotically as n and T go to zero.

Finally, we consider some results for systems at fixed z and T . We define $\gamma(r)$ by the equation

$$e(r) = \theta(r-d) + \gamma(r), \quad (9)$$

where θ is the unit step function, which we note is equal to $e(r)$ when ϕ is the pair potential for hard spheres. If we substitute Eq. (9) in the configurational partition function for the problem system and expand, we obtain a sum of N -fold integrals which can be represented by graphs with N points. In these graphs a line between points i and j stands for a factor $\gamma(r_{ij})$ in the integrand and no line between these points stands for a factor $\theta(r_{ij}-d)$. Such graphs usually contain a subgraph, call it G_m , of those m points from which a line emanates. The number of ways to choose which m points constitute G_m is the binomial coefficient

$$\binom{N}{m}.$$

Hence, we may write for the grand partition function of the problem system

$$Z_{gc} = Z_{gc,0} \left\{ 1 + \sum_{m=2}^{\infty} (m!)^{-1} \int \left[\sum_{\{G_m\}} \prod_{G_m} \gamma(r_{ij}) \theta(r_{kl}-d) \right] \times a_0^{(m)}(\mathbf{r}_1 \cdots \mathbf{r}_m) d\mathbf{r}_1 \cdots d\mathbf{r}_m \right\}, \quad (10)$$

where

$$a^{(m)}(\mathbf{r}_1 \cdots \mathbf{r}_m) = n^{(m)}(\mathbf{r}_1 \cdots \mathbf{r}_m) / \prod_{i>j} e(r_{ij}),$$

$n^{(m)}$ is the m -body density and subscript 0 refers to the hard sphere fluid. If we denote the integrand in the m th term on the right of Eq. (10) as W_m , let $W_1=0$, and define Ursell functions U_m in terms of the W_m 's in the standard fashion,¹⁵ we can take the logarithm of the right side of Eq. (10). This gives us a kind of cluster expansion for the pressure of the problem system,

$$\frac{p}{kT} = \frac{p_0}{kT} + V^{-1} \sum_{m=2}^{\infty} (m!)^{-1} \int U_m(\mathbf{r}_1 \cdots \mathbf{r}_m) d\mathbf{r}_1 \cdots d\mathbf{r}_m. \quad (11)$$

We conjecture that the leading two terms on the right

of Eq. (11) constitute a lower bound to the pressure of the problem system,

$$p/kT \geq p_0/kT + (2V)^{-1} \int [e(r) - \theta(r-d)] a_0^{(2)}(r) d\mathbf{r}_1 d\mathbf{r}_2. \quad (12)$$

We see that Inequality (12) is the analog at fixed z and T of Inequality (8). We show in the Appendix that Inequality (12) is asymptotically correct as z and T go to zero.

To complement Inequality (3), an upper bound to p is required. There is a theorem due to Groeneveld¹⁶ which has as one of its consequences

$$a_0^{(m)} \leq z^m. \quad (13)$$

If we set d equal to r_0 in Eq. (10), then every term in the sum over m is nonnegative, and we can apply Inequality (13) to obtain

$$Z_{gc} \leq Z_{gc,0} \times \left(1 + \sum_{m=2}^{\infty} \frac{z^m}{m!} \sum_{\{G_m\}} \int \prod_{G_m} \gamma(r_{ij}) \theta(r_{kl}-r_0) d\mathbf{r}_1 \cdots d\mathbf{r}_m \right). \quad (14)$$

An upper bound to Z_{gc} implies an upper bound to p . Inequality (14) suffers from a drawback of not containing a variational parameter. Furthermore, one must compute the entire series in order to obtain a rigorous upper bound. In practice one may only have to calculate a few terms for low T since the series converges rapidly there. Nevertheless, from a computational standpoint Inequality (14) is probably the least promising of the inequalities we have considered. It should be noted that Inequalities (3), (12), and (14) imply the result

$$\lim_{T \rightarrow 0} p = p_0 \text{ (fixed } z\text{)}.$$

In other words these inequalities approach the exact result as temperature decreases. They therefore represent a step beyond the inequalities which have already been derived¹⁷⁻¹⁹ for fluids with nonnegative pair potentials at fixed z and T . These already derived inequalities appear to be accurate for small z . Inequalities (3), (12) and (14) on the other hand appear to be accurate for small T .

III. COMPUTATIONS

A. Fixed N, V, S

The computations reported here are based on Inequality (2) with the hard sphere fluid as reference system. Letting Δu and Δs be the nonideal parts of the internal energy per particle and the entropy per particle respectively, we can write Inequality (2) in the form

$$\Delta u(\Delta s, n) \leq 12\xi \int_1^{\infty} \phi(xd) g_0(x; \xi) x^2 dx, \quad (15)$$

TABLE I. Internal energy of the Lennard-Jones fluid as a function of entropy and density.

n	$\Delta s^a/k$	$\Delta u/\epsilon$		d/σ
		Inequality (15)	Monte Carlo ^a	
0.4	-1.04	-2.54	-2.75	0.979
0.5	-1.34	-3.13	-3.37	0.967
0.7	-2.18	-4.34	-4.68	0.962
0.8	-2.70	-4.83	-5.25	0.960

^a L. Verlet and J.-J. Weis, Phys. Rev. **A5**, 939 (1972).

where $\xi = \frac{1}{6}\pi d^3 n$ and where d is chosen to give the reference system the same value of Δs as the problem system. We note that, unlike in the application of the Gibbs inequality at fixed n and T , the diameter d is not a variational parameter at fixed n and Δs . Thus one must settle for the accuracy obtained by using the d which the method dictates.

To treat Inequality (15) as an approximate equality has some physical basis. For a dense classical fluid one expects n and Δs , of all the thermodynamic variables, to be most closely related to the structural characteristics of the fluid.²⁰ Hence, the most reasonable choice of a hard sphere g_0 to approximate the g of the dense fluid is the g_0 which corresponds to the same n and Δs .

We now assume (15) to be an approximate equality and make use of the thermodynamic relations

$$\Delta p v = n(\partial \Delta u / \partial n)_{\Delta s},$$

$$T = \left(\frac{\partial \Delta u}{\partial \Delta s} \right) = \frac{(\partial \Delta u / \partial d)_n}{(\partial \Delta s / \partial d)_n}$$

along with the fact that fixed Δs implies fixed ξ . We thereby obtain from (15)

$$\Delta p v \approx -4\xi \int_1^\infty g_0(x; \xi) x d\phi'(xd) x^2 dx, \quad (16)$$

$$T \approx \left(12\xi \int_1^\infty \frac{\partial \xi g_0}{\partial \xi}(x; \xi) \phi(xd) x^2 dx + 4\xi \int_1^\infty g_0(x; \xi) x d\phi'(xd) x^2 dx \right) \left(\xi \frac{d\Delta s}{d\xi} \right)^{-1}. \quad (17)$$

As one would expect, Eq. (16) is the virial theorem result for $\Delta p v$.

In Table I we show calculated values of $\Delta u/\epsilon$ for various values of n ²¹ and Δs for the Lennard-Jones fluid,

$$\phi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6].$$

The hard sphere g_0 used was the solution of the Percus-Yevick equation.^{22,23} Using the Percus-Yevick expression for the Laplace transform of $xg_0(x)$, one can easily evaluate²⁴ the integrals on the right sides of (15), (16), and (17). Values of d for the hard sphere fluid were ob-

tained via the expression for Δs which follows from the equation of state of Carnahan and Starling.²⁵ Inequality (15) is only rigorous if the exact g_0 for hard spheres is used. Nevertheless, the values of Δu which we have calculated do lie above the Monte Carlo values.

In Table II we show calculated values of $\Delta u/\epsilon$ and $\Delta p v/\epsilon$ for various values of n and T . Temperature was obtained, not from Eq. (17), but by differentiation of a polynomial fit of the appropriate Δu vs Δs isochores. The high density values of Δu agree well with the Monte Carlo results. We see that $\Delta u(T)$ is obtained fairly accurately from $u(s)$ and $T = (\partial u / \partial s)_n$, even though $u(s)$ itself is not so accurate. The high density values of $\Delta p v$ are greatly overestimated. This discrepancy may be due in part to the use of the Percus-Yevick g_0 . On the other hand, the use of a more accurate g_0 entails some loss of computational ease. The low density limiting expression for $g_0(r)$ is known to be $\theta(r-d)$. One can readily show that the method we have just described does not accurately give the low density limiting values of Δu and $\Delta p v$.

B. Fixed N , V , and T

In this section we present calculations based on Inequalities (1) and (8) for the potential

$$\phi(r) = \epsilon[2(\sigma/r)^6 - 1]^2 \quad \text{for } r < 2^{1/6}\sigma,$$

$$= 0 \quad \text{for } r > 2^{1/6}\sigma. \quad (18)$$

This potential is the unperturbed potential in the perturbation theory of Weeks, Chandler, and Andersen⁶ as applied to the Lennard-Jones fluid. An accurate approximate method for obtaining the thermodynamic properties of their unperturbed system has been presented by these authors.¹² We present evidence that variational procedures based on Inequalities (1) and (8) are nearly as accurate and somewhat simpler computationally.

In Table III are values of ΔA calculated by vari-

TABLE II. Comparison of results of Inequality (15) and Eq. (16) with Monte Carlo results for the Lennard-Jones fluid.

n	T^a	$\Delta u/\epsilon$		$\Delta p v/\epsilon$		d/σ
		Inequality (15)	Monte Carlo ^b	Eq. (16)	Monte Carlo ^b	
0.5	1.35	-3.23	-3.37	-0.82	-0.94	0.970
0.85	2.889	-4.08	-4.25	10.98	9.72	0.932
0.85	2.202	-4.62	-4.76	8.10	7.04	0.947
0.85	1.128	-5.52	-5.69	2.68	2.01	0.980
0.85	0.719	-6.06	-6.12	0.02	-0.46	1.002

^a Calculation of T from Inequality (15) was done by differentiation of a polynomial fit to the calculated Δu vs Δs isochores.

^b Results for $n=0.5$ are from Footnote a of Table I. Results for $n=0.85$ are from L. Verlet, Phys. Rev. **159**, 98 (1967).

TABLE III. Helmholtz free energies of a fluid with pair potential as given by Eq. (18) calculated by variational procedures based on Inequalities (1) and (8).

T	n	$\Delta A/NkT$		d/σ		Ref. 12
		Inequality (1)	Inequality (8)	Inequality (1)	Inequality (8)	
0.75	0.84	4.68	4.34	0.995	1.022	1.022
1.35	0.40	1.29	1.15	0.982	1.003	1.005
1.35	0.65	2.55	2.37	0.975	1.001	1.003
1.36	0.50	1.68	1.57	0.979	1.002	1.004
2.81	0.85	3.48	3.20	0.932	0.968	0.970

ational procedures based on Inequalities (1) and (8). The thermodynamic functions for the reference fluid were calculated from the equation of state of Ref. 25. For the hard sphere $g_0(r)$ we took the accurate expression proposed by Verlet and Weis, and for the hard sphere $y_0(r)$ with $r < d$ we took the expression proposed in Ref. 12. Quantities calculated by the minimization of the right side of Inequality (1) are subscripted "sup"; quantities calculated by the maximization of the right side of Inequality (8) are subscripted "inf". It is first of all worth noting that the right side of Inequality (8) does have a maximum for some d , a d which is very close to the d selected by the procedure of Ref. 12. Furthermore, in all cases ΔA_{inf} lies below ΔA_{sup} . If it did not, we would have a counterexample to Inequality (8). It is also noteworthy that ΔA_{sup} and ΔA_{inf} lie close to one another. It appears, however, that ΔA_{inf} is more accurate.

In our expressions for ΔA , there is an explicit dependence on n and T and an implicit dependence on n and T via d . However, because d_{sup} and d_{inf} are chosen such that the partial derivatives of the upper and lower bound expressions with respect to d are zero, we may derive corresponding expressions for Δu and $\Delta p v$ by differentiating ΔA_{sup} and ΔA_{inf} explicitly with respect

to T and n . We obtain

$$\Delta u_{\text{sup}} = 2\pi n \int_{d_{\text{sup}}}^{r_0} \phi(r) g_{\text{sup}}(r) r^2 dr, \quad (19a)$$

$$\Delta u_{\text{inf}} = 2\pi n \int_0^{r_0} \phi(r) e(r) y_{\text{inf}}(r) r^2 dr, \quad (19b)$$

$$p_{\text{sup}} v = p_{0,\text{sup}} v + 2\pi n \int_{d_{\text{sup}}}^{r_0} \phi(r) \left(\frac{\partial n g_{\text{sup}}}{\partial n} \right) r^2 dr, \quad (20a)$$

$$p_{\text{inf}} v = p_{0,\text{inf}} v - 2\pi n \left[\int_0^{d_{\text{inf}}} e(r) \left(\frac{\partial n y_{\text{inf}}}{\partial n} \right) r^2 dr + \int_{d_{\text{inf}}}^{r_0} f(r) \left(\frac{\partial n g_{\text{inf}}}{\partial n} \right) r^2 dr \right]. \quad (20b)$$

With d chosen by the method of Ref. 12, one has additional terms due to the implicit dependence of d on n and T . Thus Eqs. (19) provide some simplification in the calculation of Δu . As can be seen from Table IV, Eq. (19b) is just about as accurate as the method of Ref. 12, which entails the numerical differentiation of ΔA vs. T isochores.

The density derivatives in Eqs. (20) present some computational difficulty. However, because d_{inf} is so close to the value of d which produces cancellation of the integral of $e(r) y_0(r)$ with the integral of $f(r) g_0(r)$, we assume that the density derivative of the sum of these

TABLE IV. Comparison of internal energies calculated from Eqs. (19) with Monte Carlo results and results of Ref. 12 for a fluid with pair potential as given by Eq. (18).

T	n	$\Delta u/kT$			Monte Carlo ^a
		Eq. (19a)	Eq. (19b)	Ref. 12	
0.75	0.84	1.04	0.99	0.98	0.97
1.35	0.40	0.18	0.18	0.18	0.17
1.35	0.65	0.49	0.47	0.46	0.46
1.36	0.50	0.27	0.27	0.27	...
2.81	0.85	0.90	0.84	0.84	0.84

^a L. Verlet and J.-J. Weis, Footnote a, Table I.

TABLE V. Comparison of compressibility factor calculated from Eq. (21) with Monte Carlo results and results of Ref. 12 for a fluid with pair potential given by Eq. (18).

T	n	$p v/kT$		
		Eq. (21)	Ref. 12	Monte Carlo ^a
0.75	0.84	10.60	10.33	10.23
1.35	0.40	2.54	2.54	2.53
1.35	0.65	4.97	4.94	4.89
1.36	0.50	3.29	3.29	3.28
2.81	0.85	7.07	6.92	6.92

^a L. Verlet and J.-J. Weis, Footnote a, Table I.

two terms is very nearly zero. Equation (20b) then simplifies to

$$p \approx p_{0,\text{int}}. \quad (21)$$

As can be seen from Table V, the simplicity of Eq. (21) is accompanied by some inaccuracy at high density.

IV. CONCLUSION

Gibbs inequalities can be formulated for the canonical, the grand canonical, and the fixed N , V , and S ensembles. If the reference system is the hard sphere fluid, then the Gibbs inequalities for the canonical and the grand canonical ensembles admit of the treatment of the hard sphere diameter d as a variational parameter. Applications of the Gibbs inequality for the canonical ensemble have already been made along these lines.^{7,8} In the case of the fixed N , V , and S ensemble the appropriate Gibbs inequality does not permit variation of d . Nevertheless, accurate results are obtainable in some, but not all, cases.

For particles with a purely repulsive pair potential with a cutoff a rigorous upper bound to the pressure at fixed activity and temperature can be derived. This bound becomes more accurate as temperature decreases. The Gibbs inequality for the grand canonical ensemble gives a lower bound to the pressure. With the hard sphere fluid as a reference system, this inequality also approaches equality as temperature decreases. Thus these two inequalities complement each other and may be useful at some of the lower temperatures of interest. It is possible, however, that calculations involving the upper bound to the pressure are only feasible at extremely low temperatures.

Finally, an inequality for a canonical ensemble of systems of particles which interact via a purely repulsive pair potential with a cutoff has been conjectured. This inequality gives a lower bound to the Helmholtz free energy. It therefore complements the Gibbs inequality. Calculations based on these inequalities have been carried out. Results appear to be nearly as accurate as the most accurate existing approximate results for purely repulsive potentials,¹² and they are obtainable with some saving of computational effort.

APPENDIX

We here consider the asymptotic behavior of the conjectured Inequalities (8) and (12), as n and T go to zero in the case of the former and as z and T go to zero in the case of the latter. To order n^2 the exact $\Delta A/NkT$ and the $\Delta A/NkT$ given by the right side of Inequality (8) are readily obtained from the standard cluster expansions¹⁵ of ΔA and $y(r)$ in powers of n . The results are

$$\begin{aligned} \frac{\Delta A}{NkT} = & -2\pi n \int_0^\infty f(r)r^2 dr - \frac{4}{3}\pi^2 n^2 \int_0^\infty f(r)r dr \\ & \times \int_0^\infty f(s) s ds \int_{|r-s|}^{r+s} f(t) t dt + \dots, \quad (A1) \end{aligned}$$

$$\begin{aligned} \frac{\Delta A}{NkT} \approx & -2\pi n \int_0^\infty f(r)r^2 dr - \frac{4}{3}\pi^2 n^2 \left[\int_0^\infty f_0(r)r dr \right. \\ & \times \int_0^\infty f_0(s) s ds \int_{|r-s|}^{r+s} f_0(t) t dt + 3 \int_0^d e(r)r dr \\ & \times \int_0^\infty f_0(s) s ds \int_{|r-s|}^{r+s} f_0(t) t dt + 3 \int_d^\infty f(r)r dr \\ & \left. \times \int_0^\infty f_0(s) s ds \int_{|r-s|}^{r+s} f_0(t) t dt \right] + \dots, \quad (A2) \end{aligned}$$

where, as in the text, subscripts 0 refer to the hard sphere system. We notice first that Eq. (A2) is exact to order n . We also notice that the term of order n^2 in Eq. (A2) is less than the corresponding term in Eq. (A1) in the special cases $d=0$, r_0 .

We subtract Eq. (A2) from Eq. (A1), divide by $\pi^2 n^2$ and call the resulting expression Δ_c . We wish to show that Δ_c is positive. We anticipate that for some d between 0 and r_0 , Δ_c will reach a minimum which at low T will fall close to r_0 . In the case $d > r_0/2$ we find after some manipulation

$$\begin{aligned} \Delta_c = & \frac{5}{18}d^6 - \frac{8}{9}r_0^3 d^3 + \frac{1}{2}r_0^4 d^2 + \frac{1}{9}r_0^6 \\ & - 4 \int_0^{r_0} e(r) \left[\frac{2}{3}(r_0^3 - d^3)r^2 - \frac{1}{2}(r_0^2 - d^2)r^3 \right] dr \\ & + 4 \int_0^{r_0} e(r)r dr \int_0^{r_0} e(s) s ds \int_{|r-s|}^{\text{lesser of } r+s, r_0} t dt \\ & - \frac{4}{3} \int_0^{r_0} e(r)r dr \int_0^{r_0} e(s) s ds \int_{|r-s|}^{\text{lesser of } r+s, r_0} e(t) t dt. \quad (A3) \end{aligned}$$

We now define I_k and ϵ as follows:

$$\begin{aligned} I_k & \equiv r_0^{-k} \int_0^{r_0} (r_0 - r)^{k-1} e(r) dr, \\ \epsilon & \equiv (r_0 - d)/r_0. \end{aligned}$$

Because $e(r)$ is small except for r near r_0 , I_k is of order I_1^k .

In terms of the I_k 's and ϵ we have

$$\begin{aligned} \Delta_c(\epsilon)/r_0^6 = & 2\epsilon^2 - (14/3)\epsilon^3 + (25/6)\epsilon^4 - (5/3)\epsilon^5 \\ & + (5/18)\epsilon^6 - 4\epsilon \left[\frac{2}{3}(3 - 3\epsilon + \epsilon^2)(I_1 - 2I_2 + I_3) \right. \\ & - \frac{1}{2}(2 - \epsilon)(I_1 - 3I_2 + 3I_3 - I_4)] + 2I_1^2 - 4I_2I_1 \\ & - 4I_3I_1 + 6I_2^2 - 4I_3I_2 + 4I_4I_1 + 4I_3^2 - 4I_4I_2 \\ & \left. - \frac{4}{3}I_1^3 + 4I_2I_1^2 - 4I_2^2I_3 + \frac{4}{3}I_3^3 + O[\exp(-\tau^{-1})] \quad (A4) \end{aligned}$$

where τ is an appropriate reduced temperature. Any integral in which the upper limit is less than r_0 can be regarded as of order $\exp(-\tau^{-1})$. We notice that I_1 is the natural temperature variable in Eq. (A4) if one neglects the exponential terms. Now let ϵ_m be the value of ϵ which minimizes Δ_c . To determine ϵ_m , we expand as

follows:

$$\epsilon_m = \epsilon_1 + \epsilon_2 + \dots + \epsilon_k + \dots, \quad (\text{A5})$$

where ϵ_k is of order I_1^k . Differentiating Eq. (A4) with respect to ϵ , substituting Eq. (A5) for ϵ_m and equating terms of order I_1 to zero, we obtain

$$\epsilon_1 = I_1. \quad (\text{A6})$$

Terms of order I_1^2 then vanish with

$$\epsilon_2 = \frac{1}{2}I_1^2 - I_2. \quad (\text{A7})$$

Substituting Eqs. (A6) and (A7) into (A4), we find

$$\Delta(\epsilon_m)/r_0^6 = 4\epsilon_2^2 + O(I_1^5) + O[\exp(-\tau^{-1})].$$

Here, with d chosen to maximize the right side of Inequality (8), the first term in the density-temperature expansion of this expression which differs from a term in the exact density-temperature expansion of A/NkT is the term in n^2T^4 . Furthermore, Eq. (A2) gives an expression for this term which lies below the exact expression.

We may also calculate the value of d which causes cancellation of the last two terms in brackets on the right side of Eq. (A2). This is the value of d , call it d_0 , which one would select in the approximate procedure of Ref. 12. We make the expansion

$$1 - d_0/r_0 = \delta_1 + \delta_2 + \dots + \delta_k + \dots,$$

where $\delta_k = O(I_1^k)$, and we find

$$\delta_1 = \epsilon_1,$$

$$\delta_2 = \epsilon_2/5,$$

$$\Delta_c(1 - d_0/r_0)/r_0^6 = 5.28\epsilon_2^2 + O(I_1^5) + O[\exp(-\tau^{-1})].$$

Hence, the method of Ref. 12 is accurate to the same order as is the variational method.

Finally, we consider Inequality (12). For $d=0$ this inequality becomes

$$p/kT \geq z + b_2z^2 \quad (\text{A8})$$

where b_k is the coefficient of z^k in the exact activity expansion of p/kT . We see that Inequality (A8) is just the $L=2$ case of the hierarchy of Inequalities (7.6) in Ref. 18. We let $\pi^2\Delta_0$ be the contribution to b_3 which is not included in the right side of Inequality (12). From the cluster expansions¹⁵ of p/kT and $y(r)$ in

powers of z we obtain

$$\Delta_0 = 8 \left(\int_0^{\tau_0} [e(r) - \theta(r-d)] r^2 dr \right)^2 - \Delta_c.$$

Proceeding as before, we find

$$\epsilon = I_1,$$

$$\epsilon_2 = (7/3)(\frac{1}{2}I_1^2 - I_2),$$

$$\Delta g(\epsilon_m)/r_0^6 = (8/3)(\frac{1}{2}I_1^2 - I_2)^2 + O(I_1^5) + O[\exp(-\tau^{-1})].$$

Hence, with d properly chosen, Inequality (12) gives exactly the leading terms in the activity-temperature expansion of p/zkT up to the term of order z^2T^4 , and it underestimates this term.

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