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Statistical theory for the entropy of a liquid

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A correlation expansion for the entropy of a classical monatomic liquid has been found to give an accurate account of the entropy for liquid sodium and for liquid argon. Here, this correlation expansion is given a conceptually simple derivation in the grand-canonical ensemble. The one- and two-particle terms together are shown to accurately represent the entropy of the hard-sphere liquid. The simplicity of the theory suggests a model for an "ideal liquid," whose free energy takes on an especially simple form. The correlation expansion for the entropy is compared in detail with previous related work.

I. INTRODUCTION

A liquid can be characterized by two conditions: there is no long-range order, and density fluctuations are small. More precisely, the first condition means there exists a correlation length l_c, of microscopic dimension, such that configurational correlations vanish among particles separated by distances greater than l_c. In the present work we assume this property holds for an equilibrium liquid; Lebowitz and Percus[1] have noted that the justification represents a fundamental problem in the theory of liquids. The second condition is made precise by introducing α, the measure of density fluctuations in a homogeneous fluid,

$$\alpha=\frac{\rho k_B T}{B_T} , \tag{1}$$

where ρ is particle density, T is temperature, and B_T is the isothermal bulk modulus. We characterize a liquid by the condition $\alpha \ll 1$. This condition delineates a region in phase space near the solid-liquid boundary;[2] in contrast, $\alpha \approx 1$ for the gas region, and $\alpha \gg 1$ for the critical region.

Based on this characterization, we have recently constructed a statistical expression for the entropy of a monatomic liquid.[3] This expression is in the form of a multiparticle correlation series,

$$S=S^{(1)}+S^{(2)}+S^{(3)}+\cdots , \tag{2}$$

which we assume to converge rapidly for a liquid. In units of k_B per particle, the one-particle term $S^{(1)}$ is the ideal-gas entropy minus 1. For liquid sodium, the first two terms alone, $S^{(1)}+S^{(2)}$, reproduce the experimental entropy to an accuracy of 1% over a wide range of temperatures.[4] For liquid argon at 85 K, $S^{(1)}+S^{(2)}$ is less than the experimental entropy by 6%;[2] one expects that this small difference represents three-particle correlations, as expressed by the term $S^{(3)}$. So far, then, the test of expression (2) for liquids is quite satisfactory.

The construction of the formula (2) proceeded by the following logical process.[3] First the correlational series was derived for the canonical ensemble. It was then observed that the multiparticle terms are nonlocal, since the configuration integrals have significant contributions from the entire volume of the liquid, and that this nonlocality can be eliminated by transforming to the grand-canonical ensemble. This transformation was effected by neglecting density fluctuations. We are now able to provide a conceptually simpler derivation, entirely within the grand-canonical ensemble. This derivation is given in Sec. II. In Sec. III we compare $S^{(1)}+S^{(2)}$ with the total entropy for the hard-sphere fluid, in both gas and liquid regimes. Some properties of our liquid entropy theory are discussed in Sec. IV, and a detailed comparison is made with a previous formulation which was designed to apply to gas and liquid regimes alike.[5-9]

II. MULTIPARTICLE CORRELATION EXPANSION OF THE ENTROPY

We first consider a canonical ensemble of mechanical systems. Each system contains N particles in a volume V, with Hamiltonian H_N given by

$$H_N=\sum_{\kappa=1}^{N}\frac{\mathbf{p}_\kappa^2}{2m}+\Phi_N . \tag{3}$$

The particles have mass m, momenta $\mathbf{p}_\kappa$, positions $\mathbf{r}_\kappa$, and the total system potential is $\Phi_N(\mathbf{r}_1,\ldots,\mathbf{r}_N)$. The partition function is Z_N,

$$Z_N=\frac{1}{h^{3N}N!}\int\cdots\int e^{-\beta H_N}d\mathbf{r}_1 d\mathbf{p}_1\cdots d\mathbf{r}_N d\mathbf{p}_N , \tag{4}$$

where $\beta=(k_B T)^{-1}$. The ensemble probability density that phase point $\mathbf{r}_1,\mathbf{p}_1,\ldots,\mathbf{r}_n,\mathbf{p}_n$ is occupied is $f_N^{(n)}(\mathbf{r}_1,\mathbf{p}_1,\ldots,\mathbf{r}_n,\mathbf{p}_n)$. For $n=N$, the probability density is

$$f_N^{(N)}=\frac{e^{-\beta H_N}}{h^{3N}Z_N} . \tag{5}$$

For $n<N$, it follows that

$$f_N^{(n)}(\mathbf{r}_1,\mathbf{p}_1,\ldots,\mathbf{r}_n,\mathbf{p}_n)=\frac{1}{(N-n)!}\int\cdots\int f_N^{(N)}(\mathbf{r}_1,\mathbf{p}_1,\ldots,\mathbf{r}_N,\mathbf{p}_N)d\mathbf{r}_{n+1}d\mathbf{p}_{n+1}\cdots d\mathbf{r}_N d\mathbf{p}_N\ . \tag{6}$$

For $n>N$, $f_N^{(n)}=0$. The expression (5) can be factored as

$$f_N^{(N)}(\mathbf{r}_1,\mathbf{p}_1,\ldots,\mathbf{r}_N,\mathbf{p}_N)=f_N^{(1)}(\mathbf{p}_1)\cdots f_N^{(1)}(\mathbf{p}_N)g_N^{(N)}(\mathbf{r}_1,\ldots,\mathbf{r}_N)\ , \tag{7}$$

where $f_N^{(1)}$ is the one-particle probability density,

$$f_N^{(1)}(\mathbf{p})=\rho_N(\beta/2\pi m)^{3/2}\exp(-\beta\mathbf{p}^2/2m)\ , \tag{8}$$

and $\rho_N=N/V$ is the number density of particles. The N-particle correlation function $g_N^{(N)}$ is defined by Eq. (7), and has the normalization

$$N!=\rho_N^N\int\cdots\int g_N^{(N)}(\mathbf{r}_1,\ldots,\mathbf{r}_N)d\mathbf{r}_1\cdots d\mathbf{r}_N\ . \tag{9}$$

The n-particle correlation function $g_N^{(n)}$ follows from (6), in the form

$$\rho_N^n g_N^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n)=\frac{\rho_N^N}{(N-n)!}\int\cdots\int g_N^{(N)}(\mathbf{r}_1,\ldots,\mathbf{r}_N)d\mathbf{r}_{n+1}\cdots d\mathbf{r}_N\ . \tag{10}$$

We now want to describe a liquid in equilibrium at density ρ and temperature T. In a small volume V in the interior of the liquid, the number of particles N will fluctuate about the mean number $\langle N\rangle=\rho V$. This density fluctuation is accounted for in the grand-canonical ensemble. Following Gibbs,[10] this ensemble may be viewed as a collection of canonical ensembles, weighted with factors $\exp(\beta\mu N)$, where μ is the chemical potential. The grand-canonical partition function is

$$Z=\sum_N e^{\beta\mu N}Z_N\ . \tag{11}$$

For a dynamical variable A, with canonical average A_N, the grand-canonical average is

$$\langle A\rangle=\sum_N\gamma_N A_N\ , \tag{12}$$

where

$$\gamma_N=\frac{e^{\beta\mu N}Z_N}{Z}\ . \tag{13}$$

We have $\sum_N\gamma_N=1$, and $\sum_N N\gamma_N=\langle N\rangle$, and the measure of density fluctuations α of Eq. (1) satisfies

$$\langle(N-\langle N\rangle)^2\rangle=\alpha\langle N\rangle\ . \tag{14}$$

In the grand-canonical ensemble, the one-particle probability density is

$$f^{(1)}(\mathbf{p})=\rho(\beta/2\pi m)^{3/2}\exp(-\beta\mathbf{p}^2/2m)\ , \tag{15}$$

and the n-particle correlation function is given by

$$\rho^n g^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n)=\sum_N\gamma_N\rho_N^n g_N^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n)\ . \tag{16}$$

Let us refer to the correlation which is present in an n-particle cluster, and which is not present in any smaller cluster, as the irreducible part of the n-particle correlation. Accordingly, the irreducible part of $g^{(2)}$ is $g^{(2)}$. The irreducible part of $g^{(3)}$ is $\delta g^{(3)}$, defined by the expression

$$g^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=g^{(2)}(\mathbf{r}_1,\mathbf{r}_2)g^{(2)}(\mathbf{r}_1,\mathbf{r}_3)\times g^{(2)}(\mathbf{r}_2,\mathbf{r}_3)\delta g^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\ . \tag{17}$$

The irreducible parts $\delta g^{(n)}$ are then defined sequentially, for $n\geq 4$; for example, $\delta g^{(4)}$ is defined by

$$g^{(4)}(\mathbf{r}_1,\ldots,\mathbf{r}_4)=g^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\cdots g^{(2)}(\mathbf{r}_3,\mathbf{r}_4)\delta g^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\cdots\delta g^{(3)}(\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4)\delta g^{(4)}(\mathbf{r}_1,\ldots,\mathbf{r}_4)\ . \tag{18}$$

Feenberg[11] has shown that $g^{(2)}(\mathbf{r}_1,\mathbf{r}_2)-1$ is a local function, i.e., when $\mathbf{r}_1$ and $\mathbf{r}_2$ are separated by a large distance, $g^{(2)}(\mathbf{r}_1,\mathbf{r}_2)-1=0$. By assumption, we extend this locality property to the higher-order functions $\delta g^{(n)}$, in the following way. For two sets of particles, m and n, separated by a distance larger than the correlation length l_c, $\delta g^{(m+n)}=1$. Under the same condition, the complete correlation function satisfies $g^{(m+n)}=g^{(m)}g^{(n)}$. This is the precise statement of our assumption that correlations vanish for particles separated by distances greater than l_c, as mentioned in the Introduction.

The nonlocal properties of correlation functions in the canonical ensemble can be demonstrated by means of (16). The summand is expanded about the mean number $\langle N\rangle$, derivatives with respect to $\langle N\rangle$ are converted to derivatives with respect to ρ (since V is constant), and the expansion is inverted, to yield

$$\rho^n g_{\langle N\rangle}^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n)=\rho^n g^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n)-\frac{\alpha}{2\langle N\rangle}\rho^2\frac{\partial^2}{\partial\rho^2}[\rho^n g^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n)]+O\left[\frac{\alpha^2}{\langle N\rangle^2}\right]\ . \tag{19}$$

The limiting behavior of $g^{(n)}_{\langle N\rangle}$, when particles are separated by distances larger than l_c, now follows from the corresponding behavior of $g^{(n)}$. For example, when $|\mathbf{r}_2-\mathbf{r}_1|>l_c$,

$$g^{(2)}_{\langle N\rangle}(\mathbf{r}_1,\mathbf{r}_2)-1=-\frac{\alpha}{\langle N\rangle} \ . \tag{20}$$

The general result for $g^{(m+n)}_{\langle N\rangle}$, when the sets m and n are separated by a distance greater than l_c, is the same as that expressed in Eq. (2.22), or (3.23), of Lebowitz and Percus.[1] The important point is that certain configuration integrals in the canonical ensemble, such as

$$\int [g^{(2)}_{\langle N\rangle}(|\mathbf{r}_1-\mathbf{r}_2|)-1]d\mathbf{r}_2 \ ,$$

or

$$\int \ln[g^{(2)}_{\langle N\rangle}(|\mathbf{r}_1-\mathbf{r}_2|)]d\mathbf{r}_2 \ ,$$

are "nonlocal," in that they contain a significant contribution from the entire volume of the system, by virtue of the large-separation property (20). This situation results from the failure of the canonical ensemble to account for density fluctuations, and under normal conditions (away from the critical point), such a nonlocal contribution to a thermodynamic function is physically incorrect. Hence in constructing a statistical expression for the entropy of a liquid, we must ensure that nonlocal terms are not present. We also note the expansion (19) is appropriate only for small n; the term linear in α, for example, contains a contribution proportional to $n(n-1)/\langle N\rangle$. When n is large, of the order of $\langle N\rangle$, the canonical and grand-canonical correlation functions presumably differ by something still of order $\langle N\rangle^{-1}$.

It is now straightforward to construct the correlation expansion for the entropy of a liquid. The grand-canonical entropy S is expressible as a sum of canonical contributions:

$$S=\sum_N \gamma_N S_N \ , \tag{21}$$

where

$$S_N=-\frac{k_B}{N!}\int\cdots\int f_N^{(N)}\ln(h^{3N}f_N^{(N)})d\mathbf{r}_1 d\mathbf{p}_1\cdots d\mathbf{r}_N d\mathbf{p}_N \ . \tag{22}$$

$f_N^{(N)}$ is factored, according to (7), and S_N becomes

$$S_N=-k_B V\int f_N^{(1)}(\mathbf{p})\ln[h^3 f_N^{(1)}(\mathbf{p})]d\mathbf{p} -k_B\frac{\rho_N^N}{N!}\int\cdots\int g_N^{(N)}\ln(g_N^{(N)})d\mathbf{r}_1\cdots d\mathbf{r}_N \ . \tag{23}$$

The important terms in (21) are at $N\approx\langle N\rangle$, where to order $\langle N\rangle^{-1}$, $g_N^{(N)}=g^{(N)}$. We use this in (23) to replace $\ln g_N^{(N)}$ by $\ln g^{(N)}$, and we use the factorization of $g^{(N)}$, defined by the continuation of (17) and (18) to $n=N$, to write $\ln g^{(N)}$ in the integrand in the form

$$\ln[g^{(N)}(\mathbf{r}_1,\ldots,\mathbf{r}_N)]=\tfrac{1}{2}N(N-1)\ln[g^{(2)}(\mathbf{r}_1,\mathbf{r}_2)]+\frac{1}{3!}N(N-1)(N-2)\ln[\delta g^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)]+\cdots \ . \tag{24}$$

The configuration integrals over $N-n$ particles are carried out with the aid of (10), the sum over N is evaluated with the aid of (16), and S is transformed to the series shown in (2). In units of k_B per particle, and correct to relative order $\langle N\rangle^{-1}$, the terms are

$$S^{(1)}=-\rho^{-1}\int f^{(1)}(\mathbf{p})\ln[h^3 f^{(1)}(\mathbf{p})]d\mathbf{p} \ , \tag{25}$$

$$S^{(2)}=-\frac{\rho}{2}\int g^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\ln[g^{(2)}(\mathbf{r}_1,\mathbf{r}_2)]d\mathbf{r}_2 \ , \tag{26}$$

$$S^{(n)}=-\frac{\rho^{n-1}}{n!}\int\cdots\int g^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n)\ln[\delta g^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n)]d\mathbf{r}_2\cdots d\mathbf{r}_n \ . \tag{27}$$

Neglecting surface effects, the integrals in $S^{(n)}$ for $n\geq 2$ are independent of $\mathbf{r}_1$. Further, these integrals are local, since $\ln g^{(2)}$, and $\ln\delta g^{(n)}$ for $n\geq 3$, are all local functions. Our basic assumption for the liquid state, i.e., for $\alpha\ll 1$, is that the n-particle irreducible correlations quickly become less important as n increases, so that the series $S^{(1)}+S^{(2)}+\cdots$ converges rapidly.

III. EVALUATION FOR THE HARD-SPHERE FLUID

An accurate equation of state for the hard-sphere fluid has recently been published by Erpenbeck and Wood.[12] From this equation of state, we calculated $S-S^{(1)}$ as a function of the dimensionless density parameter $\rho\sigma^3$, where σ is the hard-sphere diameter. The results are listed in Table I, for values of $\rho\sigma^3$ up to 0.9, which is close to the solid-liquid phase boundary. Our estimated error in the tabulated values of $S-S^{(1)}$ is $\lesssim 0.01$.

Since $g^{(2)}(\mathbf{r}_1,\mathbf{r}_2)=g^{(2)}(|\mathbf{r}_1-\mathbf{r}_2|)$ for an equilibrium fluid, the two-particle correlation entropy is

$$S^{(2)}=-\tfrac{1}{2}\rho\int g^{(2)}(|\mathbf{s}|)\ln[g^{(2)}(|\mathbf{s}|)]d\mathbf{s} \ . \tag{28}$$

Also, $g^{(2)}(|\mathbf{s}|)$ satisfies the normalization integral

$$\rho\int[g^{(2)}(|\mathbf{s}|)-1]d\mathbf{s}=-1+\alpha \ . \tag{29}$$

In these integrals, $g^{(2)}(|\mathbf{s}|)$ may be taken from experiment, say, from neutron scattering measurements in the case of a real liquid, or else from calculations in the

TABLE I. Contributions to the entropy for the hard-sphere fluid, as functions of the density. All entropy contributions are in units of k_B per particle. The liquid regime is specified by the condition $\alpha \ll 1$.

$\rho\sigma^3$	α	$S-S^{(1)}$	$S^{(2)}$	$S-S^{(1)}-S^{(2)}$
0.1	0.66	0.78	−0.04	0.82
0.2	0.44	0.52	−0.15	0.67
0.4	0.20	−0.13	−0.55	0.42
0.5	0.13	−0.55	−0.85	0.30
0.6	0.087	−1.05	−1.24	0.19
0.7	0.057	−1.66	−1.77	0.11
0.8	0.037	−2.41	−2.52	0.11
0.86	0.028	−2.96	−3.12	0.16
0.90	0.023	−3.37	−3.62	0.25

grand-canonical ensemble, and the integrands are local. However, from (19), the canonical and grand-canonical correlation functions differ locally by order $\langle N\rangle^{-1}$, so to this order of accuracy, the canonical function $g^{(2)}_{\langle N\rangle}(|\mathbf{s}|)$ can be used, provided the integrals are cut off at an upper value of $|\mathbf{s}|\approx l_c$. The best available values of the correlation function for hard spheres are those of Verlet and Weis,[13] which are based on an analytic solution of the Percus-Yevick equation (grand canonical), plus corrections at high densities from Monte Carlo calculations for systems of 864 hard spheres (canonical). The Verlet-Weis prescription is expressed in a program by Henderson, which is listed in Appendix D of McQuarrie.[14] At the highest densities, $\rho\sigma^3 \geq 0.8$, the integrals in (28) and (29) are poorly converged at the upper limit $|\mathbf{s}|=5\sigma$, which is the limit of the Verlet-Weis data; hence at high densities we used (29) to estimate a remainder for (28). The results for $S^{(2)}$ are listed in Table I.

Let us examine the results in Table I. As $\rho\sigma^3 \rightarrow 0$, $\alpha \rightarrow 1$, $S-S^{(1)} \rightarrow 1$, and $S^{(2)} \rightarrow 0$: all these functions for the hard-sphere fluid approach the correct limits for an ideal gas. The present entropy theory is obviously not valid for a gas. On the other hand, at high densities, α becomes small compared to 1, and our liquid entropy theory is valid. For $\rho\sigma^3=0.6-0.9$, the first two terms $S^{(1)}+S^{(2)}$ express the total entropy of the hard-sphere liquid to 0.17 rms deviation. The error in $S^{(2)}$, ultimately due to finite-system limitations of the Monte Carlo calculations,[13] is possibly of the same order. Hence we can only say that $S^{(3)}$ is probably of the order 0.1–0.2 for the hard-sphere liquid.

IV. DISCUSSION

The integral in (25) is evaluated to give

$$S^{(1)}=\tfrac{3}{2}-\ln(\rho\Lambda^3) , \tag{30}$$

where $\Lambda=\hbar(2\pi\beta/m)^{1/2}$ is the de Broglie wavelength. In the limit $\rho \rightarrow 0$, or $\beta \rightarrow 0$, each correlation contribution $S^{(n)}$ approaches zero, for small n. However, the entropy of an ideal gas is not $S^{(1)}$, but $S^{(1)}+1$. Why does this 1 not appear in our correlation expansion of the entropy? Because we lost it by dropping the high-order configuration terms. This can be seen by using the ideal-gas value $N!N^{-N}$ for $g_N^{(N)}$ in (23), and (21), to find the configuration contribution $\langle N\rangle k_B$, or 1 in units of k_B per particle. Hence our correlation expansion is not appropriate for a gas, because in this expansion the ideal-gas configuration entropy of 1 appears in the orders $n\approx\langle N\rangle$.

The correlation expansion of the canonical entropy was first given by H. S. Green.[5] The nonlocality of the canonical entropy was recognized by Nettleton and M. S. Green,[6] who transformed the theory to the grand-canonical ensemble. A cumulant expansion of the Nettleton and Green theory was written out, through four-particle terms, by Yvon.[7] An alternate derivation was given by Raveché,[8] who expressed the entropy as a power series in ρ, which he showed to be identical to Nettleton and Green to fourth order, and which he presumed to be identical to Nettleton and Green to all orders. In a companion paper, Mountain and Raveché[9] evaluated contributions for the hard-sphere fluid. Because the latter authors were able to include part, but not all, of the third-order terms for hard spheres, it is not meaningful to compare their numbers with the numbers in Table I. Instead, we will compare the present correlation expansion with the theory of Refs. 5–9, order by order.

Equation (V.1) of Raveché[8] expresses the entropy relative to the ideal-gas value of $S^{(1)}+1$; the first two correlational terms are written out explicitly in (V.3). Each correlation term contains the irreducible part $S^{(n)}$, given by (27), plus a cumulant expression. The cumulant in the second-order term is

$$\tfrac{1}{2}\rho\int(g^{(2)}-1)d\mathbf{s} ,$$

which can be evaluated with the aid of (29). Likewise, the cumulant contribution to each order can be evaluated, and in each order the entropy of Raveché has the following value: first order,

$$S^{(1)}+1 ,$$

second order,

$$S^{(2)}-\tfrac{1}{2}+\tfrac{1}{2}\alpha , \tag{31}$$

third order,

$$S^{(3)}-\tfrac{1}{6}+\tfrac{1}{2}\alpha+O(\alpha^2) ,$$

and so on. When $\rho \rightarrow 0$, or $\beta \rightarrow 0$, then $\alpha \rightarrow 1$, and the series (31) has the correct ideal-gas limit. In the liquid regime, if we neglect the small terms in α, then partial sums of the series (31) differ from partial sums of the present theory by the sequence of numbers $1,\frac{1}{2},\frac{1}{3},\ldots$. For the hard-sphere liquid, according to Table I, the present theory at the second order is considerably more accurate than $\frac{1}{2}$. However, it is still possible that this accuracy is fortuitous, hence further tests of the theory would be useful. An extension to molecular liquids, where angular correlations are present, would also be interesting.

It is of interest to note that our correlation expansion is not equivalent to the Boltzmann form,

$$-\int f^{(1)}\ln(h^3 f^{(1)})d\mathbf{p} ,$$

extended to higher order $f^{(n)}$. For example, let us write the entropy per particle in the form

$$-\frac{1}{2\langle N\rangle^2}\int\cdots\int f^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2)\ln[h^6 f^{(2)}(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2)]d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{p}_1 d\mathbf{p}_2 .$$

By factoring $f^{(2)}$ and carrying out the integrals, this becomes

$$S^{(1)}+\langle N\rangle^{-1}S^{(2)}+\mathcal{T} ,$$

where $\mathcal{T}$ represents other terms of order $\langle N\rangle^{-1}$. Hence the above form based on $f^{(2)}$ does not contain the correlation entropy $S^{(2)}$.

In discussing the entropy of a classical monatomic liquid, we have not specified the form of the total potential Φ_N, which appears in (3) for the Hamiltonian. Let us write the total potential as a multiparticle series,

$$\Phi_N=\frac{1}{2}\sum_{\kappa,\lambda=1}^{N}\phi(|\mathbf{r}_\kappa-\mathbf{r}_\lambda|)+\cdots , \tag{32}$$

where $+\cdots$ represents n-particle potentials for $n\geq 3$. To the extent that an n-particle potential is important in Φ_N, one would expect the corresponding $S^{(n)}$ to be important in the entropy. The simplest model, which captures much of the nature of real monatomic liquids, is to neglect n-particle potentials for $n\geq 3$; in this case the mean potential energy per particle becomes

$$\frac{\langle\Phi\rangle}{\langle N\rangle}=\frac{1}{2}\rho\int\phi(|\mathbf{s}|)g^{(2)}(|\mathbf{s}|)d\mathbf{s} . \tag{33}$$

Let us add the further approximation of neglecting irreducible n-particle correlations, for $n\geq 3$, so that the entropy is simply $S^{(1)}+S^{(2)}$, and refer to the resulting model as an ideal liquid. The Helmholtz free energy F, for an ideal liquid, takes on the particularly simple form

$$\frac{F}{\langle N\rangle}=k_B T\ln(\rho\Lambda^3)+\frac{1}{2}\rho\int[\phi(|\mathbf{s}|)-w^{(2)}(|\mathbf{s}|)]g^{(2)}(|\mathbf{s}|)d\mathbf{s} , \tag{34}$$

where $w^{(2)}(|\mathbf{s}|)$ is the two-particle potential of mean force, defined by

$$\ln[g^{(2)}(|\mathbf{s}|)]=-\beta w^{(2)}(|\mathbf{s}|) . \tag{35}$$

In summary, the correlation expansion (2) for the entropy of a classical monatomic liquid is conceptually simple, and the first two terms accurately represent the entropy for liquid sodium,[4] for liquid argon,[2] and as shown here, for the hard-sphere liquid as well.

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