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Surface Effects in One-Dimensional Classical Fluids with Nearest-Neighbor Interactions

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An exact study is made of the surface thermodynamic properties and grand canonical distribution functions for a one-dimensional gas of classical particles with nearest-neighbor interactions bounded by hard walls. The density profile is expressed in terms of the bulk pair correlation function. We also analyze the interface near a potential step.

I. INTRODUCTION

There are two alternative approaches to the calculation of thermodynamic surface properties of many-particle systems in thermal equilibrium.[1] In the first, one aims at calculating the partition function for a system of finite size, and one identifies the surface properties by studying its functional dependence on volume and shape. In the second approach, one studies the molecular distribution functions near the surface or interface and calculates the surface properties as averages over these functions. The latter approach naturally requires a much more detailed description, and besides the surface free energy, it also yields the density profile. Of course, when carried out exactly for a finite system both approaches give the same results for the thermodynamic properties.[2] Rather than the exact distribution functions, it is tempting, however, to use distribution functions calculated in the thermodynamic limit by letting the system become infinite in certain directions. If the concept of surface free energy per unit area has a well-defined meaning, this should make no difference.

We have studied the surface effects for an exactly soluble model of a fluid, namely, a one-dimensional system of classical particles with nearest-neighbor interactions.[3] In the finite system, the particles can move along the interval $0<x<L$ and are reflected by hard walls at $x=0$ and $x=L$. The thermodynamic limit is taken by letting L tend to infinity, and we are then interested in the boundary effects near $x=0$. The logarithm of the grand partition function for the finite system may be calculated exactly to terms of order unity. The grand canonical one- and two-particle distribution functions for the infinite system may also be calculated exactly. The thermodynamic surface properties calculated via both methods are identical.

The study of the distribution functions near a hard wall is of interest, since this situation has often been used as an idealized model of the liquid-gas interface.[4] Bellemans has derived cluster expansions for the surface properties and distribution functions near a hard wall.[5]

For the case of hard rods, Leff and Coopersmith[6] have investigated the translational invariance properties of the canonical distribution functions for the finite system. They have shown that there exists a central region, which becomes smaller as the order of the distribution function increases, in which the functions have translational invariance. These results were later extended to forces of finite range.[7] Flicker[8] has shown for hard rods that in its central region the two-particle correlation function is a constant for large separation of particles. Millard[9] has investigated the grand canonical one-particle distribution for hard rods, both for the finite system and in the thermodynamic limit.

In Sec. II, we calculate the grand partition function to the desired order. In Sec. III we study the distribution functions. As is well known, in the present model the Kirkwood superposition approximation is exact and one may calculate all higher distribution functions from the one- and two-particle functions.[10] It turns out that there is an interesting relation between the density profile and the bulk pair correlation function given by Eq. (3.20). In Sec. IV, we study the thermodynamic surface properties, namely, the particle excess and the surface energy via both methods.

Owing to the nonzero range of the interaction, one can not give a unique microscopic definition of the local pressure, but, for systems with pair interactions, Irving and Kirkwood[11] have shown that a natural definition may be found which leads to a local momentum balance equation valid on a microscopic level. This definition is easily extended to the case of nearest-neighbor interactions, and we verify explicitly that the hydrostatic equation is satisfied microscopically, i.e., the pressure is constant throughout the system. This is of interest in relation to existing theories of nonuniform fluids.[12, 13]

In Sec. VI, we analyze the case where the system extends to $x<0$ with a finite potential step at $x=0$. In this case, we find the nonuniform distribution functions and the thermodynamic properties associated with the interface. Again, the density profile is simply related to the bulk pair correlation functions on both sides of the step. In future work, we hope to use this method to study the liquid-gas interface in the one-dimensional many-body cluster interaction model.[14]

II. GRAND PARTITION FUNCTIONS

Consider a one-dimensional classical system of identical particles mass m, on the line segment $(0, L)$ bounded by hard walls. We assume nearest-neighbor interactions; i.e., the total interaction potential between N particles is given by

$$U_N(r_1,\ldots,r_N)=\sum_{i=1}^{N-1} \varphi(r_{i+1}-r_i) \quad , \tag{2.1}$$

where we have numbered the particles along the line, $0<r_1\leq r_2 \leq, \ldots, \leq r_N<L$. It is easily shown that if $\varphi(r)$ is bounded below, and if for some fixed positive R_0 and w

$$\varphi(r)\leq wr^{-(1+\epsilon)}, \quad \text{for } r>R_0, \quad \epsilon>0 \quad , \tag{2.2}$$

then the interaction satisfies stability and weak tempering conditions sufficient to ensure that the system has a proper thermodynamic limit.[15] The above conditions are also sufficient to exclude a phase transition.[16] An example of a system with interaction potential (2.1) is given by a system with pairwise interactions

$$U_N=\sum_{i<j}^{N} \varphi_2(|r_i-r_j|) \quad , \tag{2.3}$$

with a two-body potential $\varphi_2(r)$, which has a hard core with diameter a and which vanishes identically for $r\geq 2a$.

The grand canonical partition function may be written

$$\Xi(z,\beta,L)=\sum_{N=0}^{\infty} z^N \int_0^L \int_{r_1}^L \cdots \int_{r_{N-1}}^L \times\exp(-\beta U_N)dr_1 dr_2, \ldots, dr_N \quad , \tag{2.4}$$

where, in standard notation,

$$\beta=1/k_BT, \; z=e^{\beta\mu}/\Lambda, \; \Lambda=(h^2/2\pi m k_BT)^{1/2} , \tag{2.5}$$

and where the first term is unity by convention. The Laplace transform with respect to L of the grand partition function

$$\Psi(z,\beta,s)=\int_0^\infty e^{-sL}\Xi(z,\beta,L)dL \tag{2.6}$$

is found to be given by

$$\Psi(z,\beta,s)=s^{-1}+s^{-2}\frac{z}{1-zJ(\beta,s)} \quad , \tag{2.7}$$

where

$$J(\beta,s)=\int_0^\infty e^{-sr-\beta\varphi(r)}dr \quad . \tag{2.8}$$

We also consider a slightly modified system in which the first particle interacts with a particle fixed at the origin (we shall call this the O system). The total interaction potential for an O system with N particles is

$$U_N^{O}(r_1,\ldots,r_N)=U_N(r_1,\ldots,r_N)+\varphi(r_1) . \tag{2.9}$$

The Laplace transform of its grand partition function $\Xi^{O}(z,\beta,L)$ is given by

$$\Psi^{O}(z,\beta,s)=s^{-1}\frac{1}{1-zJ(\beta,s)} \quad . \tag{2.10}$$

Inverting the Laplace transforms (2.7) and (2.10) one finds

$$\Xi(z,\beta,L)=[-s_0^2J_{;s}(\beta,s_0)]^{-1}e^{s_0L}[1+o(e^{-\lambda L})] \quad ,$$
$$\Xi^{O}(z,\beta,L)=[-s_0zJ_{;s}(\beta,s_0)]^{-1}e^{s_0L}[1+o(e^{-\lambda L})] \quad , \tag{2.11}$$

where $s_0(z,\beta)$ is the root with largest real part of

$$1=zJ(\beta,s) \quad . \tag{2.12}$$

The subscript ; s in (2.11) denotes partial differentiation with respect to s at constant β. Finally, λ is given by

$$\lambda(z,\beta)=s_0-\mathrm{Re}\,s_1-\epsilon \quad , \tag{2.13}$$

where ϵ is small and positive and where $s_1(z,\beta)$ is the singularity with next largest real part of

(2.7) and (2.10). If s_1 is real, one may show[17] that $s_1 = 0$. From (2.11), it follows that the grand potential of the system is given by

$$q(z, \beta, L) = \ln \Xi(z, \beta, L) = s_0 L - \ln[-s_0{}^2 J_{;s}(\beta, s_0)] + o(e^{-\lambda L}). \tag{2.14}$$

A similar expression holds for the O system. In the thermodynamic limit, the first term in (2.14) dominates, so that the bulk pressure $p(z, \beta)$ of the system is given by

$$s_0 = \beta p \ . \tag{2.15}$$

The energy per particle e and the particle density ρ follow from the thermodynamic relation

$$ds_0 = \rho d(\beta\mu) - \rho e d\beta = \rho d \ln z - \rho(e - \tfrac{1}{2} k_B T) d\beta \ . \tag{2.16}$$

The second term in (2.14) represents the boundary effects. We may call

$$\psi(z, \beta) = -\ln[-s_0{}^2 J_{;s}(\beta, s_0)] \tag{2.17}$$

the *surface grand potential.* It is related to the *surface tension* γ of a single surface by

$$\psi(z, \beta) = -2\beta\gamma \ . \tag{2.18}$$

III. DISTRIBUTION FUNCTIONS

The probability density for finding the first particle of the system at a distance x from the origin is defined by

$$P_1(x; z, \beta, L) = [\Xi(z, \beta, L)]^{-1} \sum_{N=1}^{\infty} z^N \int_0^L \cdots \int_{r_{N-1}}^L \delta(r_1 - x) \exp(-\beta U_N) dr_{1, \ldots,} dr_N \ . \tag{3.1}$$

It is obviously given by (in simplified notation)

$$P_1(x; L) = z \Xi^O(L - x)/\Xi(L) = s_0 e^{-s_0 x}[1 + o(e^{-\lambda(L - x)})] \ . \tag{3.2}$$

Henceforth we shall drop the subscript zero in s_0. In the thermodynamic limit $L \to \infty$ one has

$$P_1(x) = \lim_{L \to \infty} P_1(x; L) = s e^{-sx} \ . \tag{3.3}$$

Similarly, the probability density for finding the first two particles at x_1 and x_2, respectively, is given by

$$P_{1,2}(x_1, x_2; L) = z^2 e^{-\beta\varphi(x_2 - x_1)} \Xi^O(L - x_2)/\Xi(L) = z s e^{-s x_2 - \beta\varphi(x_2 - x_1)}[1 + o(e^{-\lambda(L - x_2)})] \tag{3.4}$$

In the thermodynamic limit, one finds

$$P_{1,2}(x_1, x_2) = P_1(x_1) N(x_2 - x_1) \ , \tag{3.5}$$

where $N(r)$ is the nearest-neighbor distribution

$$N(r) = e^{-sr - \beta\varphi(r)}/J(\beta, s) \ , \tag{3.6}$$

and where we have made use of (2.12). Continuing the above procedure one finds for the joint probability distribution of the first n particles in the limit $L \to \infty$

$$P_{1,\ldots,n}(x_1, \ldots, x_n) = P_1(x_1) N(x_2 - x_1) \cdots N(x_n - x_{n-1}) \ . \tag{3.7}$$

Hence the nearest-neighbor distribution serves as the conditional probability in a Markov chain.[10, 18] Obviously,

$$P_{j+1}(x) = \int_0^x N(x - y) P_j(y) dy \ , \tag{3.8}$$

where $P_j(y)$ is the probability density of the jth particle at y. On account of the convolution nature of this process it is convenient to take Laplace transforms and to define

$$\tilde{P}_j(\xi) = \int_0^\infty e^{-\xi x} P_j(x) dx \ . \tag{3.9}$$

From (3.8), it follows that

$$\tilde{P}_{j+1}(\xi) = \tilde{N}(\xi) \tilde{P}_j(\xi) \ . \tag{3.10}$$

From (3.6), we have explicitly

$$\tilde{N}(\xi) = J(\beta, s + \xi)/J(\beta, s) = J[\xi]/J \ , \tag{3.11}$$

where the second equality defines a convenient notation.

The density profile in the thermodynamic limit is defined by

$$\rho(x)=\sum_{i=1}^{\infty} P_i(x) \ . \tag{3.12}$$

After Laplace transformation, we find from (3.10)

$$\tilde{\rho}(\xi)=\frac{s}{s+\xi}\ \frac{1}{1-zJ[\xi]} \ , \tag{3.13}$$

where we have used (2.12). Fisher and Bokut[19] have evaluated the sum of the first eight terms in (3.12) numerically for hard-core square-well pair interactions. As is evident from (2.10) the density profile may be simply expressed in terms of the partition function of a finite O system.[9]

The probability distribution $P_{i,j}(x, x+r)$ for finding particle i at x and particle j at a positive distance r has a Laplace transform

$$\tilde{P}_{i,j}(\xi,\sigma) = \int_0^{\infty} dx \int_0^{\infty} dr e^{-\xi x-\sigma r} P_{i,j}(x, x+r) \ , \tag{3.14}$$

which is easily found to be given by

$$\tilde{P}_{i,j}(\xi,\sigma)=\frac{s}{s+\xi}\ (zJ[\xi])^{i-1}(zJ[\sigma])^{j-i} \ . \tag{3.15}$$

Hence, the pair distribution in the thermodynamic limit, defined (for $r>0$) by

$$\rho_2(x|r)=\sum_{i=1}^{\infty}\ \sum_{j=i+1}^{\infty} P_{i,j}(x, x+r) \ , \tag{3.16}$$

has the Laplace transform

$$\tilde{\rho}_2(\xi,\sigma)=\frac{s}{s+\xi}\ \frac{1}{1-zJ[\xi]}\ \frac{zJ[\sigma]}{1-zJ[\sigma]} \ \cdot \tag{3.17}$$

Therefore, we may write (for $r>0$)

$$\rho_2(x|r)=\rho(x)\rho g(r) \ , \tag{3.18}$$

where $g(r)$ is the pair correlation function in the bulk. From (3.17), we have

$$\rho\tilde{g}(\sigma)=\frac{zJ[\sigma]}{1-zJ[\sigma]} \ . \tag{3.19}$$

From (3.13) and (3.19) it follows that there is a simple relation between the density profile and the bulk pair correlation function, namely,

$$\rho(x)=\rho+(s-\rho)e^{-sx}+s\int_0^x \rho G(r)e^{-s(x-r)}dr \ , \tag{3.20}$$

where $G(r)=g(r)-1$. (3.21)

It should be noted that the microscopic definition (3.12) of the density profile gives rise to considerably more structure than is encountered in the usual semimacroscopic treatments.[20] In the latter theories, the density profile is always given by a monotonic function. It is clear from (3.20) that with our definition the profile will show the oscillations present in the pair correlation function. Thus in a certain region of the (p, T) plane the profile will be oscillatory even at an asymptotically large distance from the wall.[17] Recent experiments[21] of light scattering from diffuse interfaces near the critical point are in excellent agreement with the semimacroscopic theories. It should be stressed that in this type of experiment one sees only the long-wavelength Fourier components of the density profile, whereas the more detailed structure, which actually is present, is completely washed out. In principle it should be possible to study the finer details with the aid of more subtle probes.

Besides the pair distribution $\rho_2(x|r)$ we consider the neighbor pair distribution $N_2(x|r)$ defined by

$$N_2(x|r)=\sum_{i=1}^{\infty} P_{i,i+1}(x, x+r) \ . \tag{3.22}$$

From (3.15), it follows that (for $r>0$)

$$N_2(x|r)=\rho(x)N(r) \ . \tag{3.23}$$

Finally we consider the probability density $P\alpha(x, y; L)$ for finding a particle at the point $\alpha L+x$, where $x<0$ and $0<\alpha<1$, and its right-hand neighbor at the point $\alpha L+y$, where $y>0$. By the same method as before we find

$$P_\alpha(x,y;L)=z^2e^{-\beta\varphi(y-x)} \times\Xi^O(\alpha L+x)\Xi^O(L-\alpha L-y)/\Xi(L). \tag{3.24}$$

Substituting (2.11) and taking the thermodynamic limit $L\to\infty$, we obtain

$$P_\alpha(x,y)=-J_{;s}^{-1}\exp[s(x-y)-\beta\varphi(y-x)] \ . \tag{3.25}$$

This is just the neighbor pair distribution in the bulk of the system, as may be seen by taking the limit $x\to\infty$ in (3.23) and using (3.6) and (4.2).

IV. SURFACE THERMODYNAMICS

In this section, we wish to investigate how the average properties of the boundary layer in the thermodynamic limit $L\to\infty$ are related to the higher-order terms in the grand partition function (2.14). Firstly, we consider the *particle excess* Γ, defined by

$$\Gamma = \int_0^\infty [\rho(x) - \rho]\,dx \; . \tag{4.1}$$

This is easily obtained from the Laplace transform (3.13). From (2.12) and (2.16), it follows that the bulk density ρ is given by

$$\rho = -J/J_{;s} \; . \tag{4.2}$$

Hence, we find

$$\begin{aligned} \Gamma &= \lim_{\xi \to 0} \left(\frac{s}{s+\xi}\, \frac{1}{1 - zJ[\xi]} + \frac{J}{\xi J_{;s}} \right) , \\ \Gamma &= \frac{J}{sJ_{;s}} + \frac{1}{2}\, \frac{JJ_{;ss}}{J_{;s}^{\,2}} \; . \end{aligned} \tag{4.3}$$

From (4.2), we have

$$\left(\frac{\partial \rho}{\partial s} \right)_\beta = -1 + \frac{JJ_{;ss}}{J_{;s}^{\,2}} \; , \tag{4.4}$$

so that

$$\Gamma = \frac{1}{2} \left(\frac{\partial \rho}{\partial s} \right)_\beta + \frac{1}{2} - \frac{\rho}{s} \; . \tag{4.5}$$

This result may be checked by integrating (3.20) directly and using the compressibility theorem[22]

$$\int_0^\infty \rho G(r)\,dr = \frac{1}{2} \left(\frac{\partial \rho}{\partial s} \right)_\beta - \frac{1}{2} \; . \tag{4.6}$$

Some more care is needed in the definition of the surface energy. The total energy of the finite system is given by

$$\begin{aligned} E(z, \beta, L) = {} & \tfrac{1}{2} k_B T \int_0^L \rho(x; z, \beta, L)\,dx \\ & + \tfrac{1}{2} \int_0^L dx \int_0^L dy\, \varphi(|x-y|) N_2(x, y; z, \beta, L) \; , \end{aligned} \tag{4.7}$$

where $N_2(x, y; L)$ is the neighbor distribution for the finite system. Subtracting the bulk energy for a system of size L,

$$\begin{aligned} L\rho e &= L\rho(\tfrac{1}{2} k_B T + \langle \varphi \rangle) \\ &= \tfrac{1}{2} k_B T \int_0^L \rho(z, \beta)\,dx + \int_0^L dx \int_0^\infty \rho N(r) \varphi(r)\,dr \; , \end{aligned} \tag{4.8}$$

one obtains

$$E(z, \beta, L) - L\rho e = \tfrac{1}{2} k_B T \int_0^L [\rho(x; L) - \rho]\,dx + \tfrac{1}{2} \int_0^L dx \Big[\int_0^L dy\, \varphi(|x-y|) N_2(x, y; L) - 2 \int_0^\infty \rho N(r) \varphi(r)\,dr \Big] \; . \tag{4.9}$$

With the aid of the identity

$$\tfrac{1}{2} \int_0^L dx \int_0^L dy\, \varphi(|x-y|) N(|x-y|) = L \int_0^L \varphi(r) N(r)\,dr - \int_0^L r \varphi(r) N(r)\,dr \; , \tag{4.10}$$

we may rewrite the potential energy term in (4.9) as

$$\tfrac{1}{2} \int_0^L dx \int_0^L dy\, \varphi(|x-y|) [N_2(x, y; L) - \rho N(|x-y|)] - \int_0^L r \varphi(r) \rho N(r)\,dr - L \int_L^\infty \rho N(r) \varphi(r)\,dr \; . \tag{4.11}$$

We define the *surface energy* $\mathcal{E}(z, \beta)$ for a single wall by

$$\begin{aligned} \mathcal{E}(z, \beta) = {} & \tfrac{1}{2} k_B T \Gamma + \int_0^\infty dx \int_0^\infty \varphi(r) [N_2(x|r) - \rho N(r)] \\ & - \tfrac{1}{2} \rho \int_0^\infty r \varphi(r) N(r)\,dr \; . \end{aligned} \tag{4.12}$$

Later in this section we shall prove that

$$\mathcal{E}(z, \beta) = \lim_{L \to \infty} \tfrac{1}{2} [E(z, \beta, L) - L\rho e] \; , \tag{4.13}$$

which shows that a simple-minded limiting procedure in (4.9) yields the correct expression (4.12) for the surface energy. The first term in (4.12) represents the kinetic energy of the excess of particles near the wall. The second term is the change in interaction energy due to the distortion of the pair distribution function near the wall. The last term represents the loss of interaction energy owing to the absence of particles on the other side of the wall. We shall call this term the *energy defect* $\Delta(z, \beta)$. From (3.25) and (4.2), it follows that the interaction energy across a partition in the bulk of the system is given by

$$\begin{aligned} & \int_{-\infty}^0 dx \int_0^\infty dy\, \varphi(y-x) P_\alpha(x, y) \\ & \quad = \rho \int_{-\infty}^0 dx \int_0^\infty dy\, \varphi(y-x) N(y-x) \\ & \quad = \rho \int_0^\infty r \varphi(r) N(r)\,dr = 2\Delta(z, \beta) \; , \end{aligned} \tag{4.14}$$

which justifies the above interpretation of the energy defect. On account of (3.23), the surface energy may be written

$$\mathcal{E}(z, \beta) = \Gamma e - \Delta \quad . \tag{4.15}$$

In microscopic theories of surface tension in systems with pair forces, one has often treated the liquid-gas interface approximately by neglecting the vapor side altogether and replacing the interface by the profile near a hard wall.[4] For the surface potential energy one then writes the three-dimensional analog of

$$\begin{aligned}\tfrac{1}{2} \int_0^\infty dx \int_{-\infty}^\infty dr \varphi(|r|)[\rho_2(x, x+r) - \rho^2 g(|r|)] \\ = \int_0^\infty dx \int_0^\infty dr \varphi(r)[\rho_2(x|r) - \rho^2 g(r)] \\ -\tfrac{1}{2} \int_0^\infty r\varphi(r)\rho^2 g(r) dr \quad ,\end{aligned} \tag{4.16}$$

where we have made use of the symmetry $\rho_2(x, y) = \rho_2(y, x)$ and of the fact that $\rho_2(x, y)$ vanishes identically for x or $y < 0$. In the case of pair forces, $N_2(x|r)$ and $N(r)$ in (4.12) may be replaced by $\rho_2(x|r)$ and $\rho g(r)$, respectively, and in that case, the expressions for the surface potential energy as given by (4.12) and (4.16) are identical. As a further approximation one neglects the distortion of the pair distribution, i.e., one puts

$$\rho_2(x|r) = \theta(x)\theta(x+r)\rho^2 g(r) \quad , \tag{4.17}$$

where $\theta(x)$ is the unit step function defined by

$$\begin{aligned}\theta(x) &= 1, \quad \text{for } x > 0 \quad , \\ \theta(x) &= 0, \quad \text{for } x < 0 \quad .\end{aligned} \tag{4.18}$$

As is evident from the right-hand side in (4.16), the surface potential energy then becomes equal to minus the energy defect. Kirkwood and Buff[4] have shown that for liquid argon far from the critical point, this procedure gives reasonably good agreement with the experimental values of surface energy and surface tension.

We return to the nearest-neighbor interaction model. It follows from (2.12) and (4.2) that the surface grand potential defined in (2.17) may be expressed entirely in terms of bulk thermodynamic properties, namely,

$$\psi(z, \beta) = \ln[z\rho/s^2] \quad . \tag{4.19}$$

It is convenient, however, to regard ψ as a function of β and s and to use (2.17) to derive

$$d\psi = -\frac{J_{;\beta s}}{J_{;s}} d\beta - \left(\frac{2}{s} + \frac{J_{;ss}}{J_{;s}}\right) ds \quad . \tag{4.20}$$

From the definition of the energy defect, we have

$$\Delta(z, \beta) = \tfrac{1}{2}\rho \int_0^\infty r\varphi(r) N(r) dr = -\tfrac{1}{2} J_{;\beta s}/J_{;s} \; , \tag{4.21}$$

where we have used (3.6) and (4.2). Using also (4.3), we may write

$$\begin{aligned}\tfrac{1}{2} d\psi &= \Delta d\beta + (\Gamma/\rho) ds \\ &= \Gamma d \ln z - (\Gamma\langle\varphi\rangle - \Delta) d\beta \quad ,\end{aligned} \tag{4.22}$$

where in the last line we have used (2.16). From (2.18), it follows that (4.22) is essentially the *Gibbs adsorption equation* for the surface tension γ. On comparing (2.16) and (4.22), one finds that the particle excess Γ may be found by differentiating $\psi(z, \beta)$ with respect to z at constant β, in the same way as the bulk density ρ may be obtained from $s(z, \beta)$. Similarly, the surface potential energy may be found by differentiating $\psi(z, \beta)$ with respect to β at constant z. We note that in the present case the energy defect Δ may be found from $\psi(z, \beta)$ by differentiation with respect to s at constant β, and may be expressed in terms of bulk thermodynamic properties via (4.19). Hence, we find

$$\Delta(z, \beta) = \frac{1}{2}\left[\left(\frac{\partial \ln\rho}{\partial\beta}\right)_s + \langle\varphi\rangle\right] \quad . \tag{4.23}$$

V. LOCAL PRESSURE

In this section, we will show that a natural microscopic definition of the local pressure may be given which has the appealing property that the pressure is constant throughout the system. First we derive the virial theorem for the bulk pressure.[23] Assuming for generality a hard-core diameter a, one has by partial integration the identity

$$\begin{aligned}\int_a^\infty e^{-sr - \beta\varphi(r)} dr = -a e^{-sa - \beta\varphi(a)} \\ + \int_{a+}^\infty r\left(s + \beta \frac{\partial\varphi}{\partial r}\right) e^{-sr - \beta\varphi(r)} dr \quad .\end{aligned} \tag{5.1}$$

Hence, $$s = \rho + aN(a)\rho - \beta\rho \int_{a+}^\infty r \frac{\partial\varphi}{\partial r} N(r) dr, \tag{5.2}$$

where we have used $\rho^{-1} = v = \langle r\rangle$. In the case of pair forces, $N(r)$ may be replaced by $\rho g(r)$, and then (5.2) is the virial theorem in its usual form. The virial theorem in the form originally derived by Clausius states that the bulk pressure as given by (5.2) is equal to the pressure on the walls. Since the latter is due purely to kinetic momentum transfer we must have

$$\rho(0) = s \quad . \tag{5.3}$$

Equation (3.20) shows that (5.3) is in fact satisfied. With the aid of the identity

$$N(a)=s+\beta\int_{a+}^{\infty}\frac{\partial\varphi}{\partial r}N(r)dr\ , \qquad (5.4)$$

one may also write

$$s=\frac{\rho}{1-\rho a}\left[1-\beta\int_{a+}^{\infty}(r-a)\frac{\partial\varphi}{\partial r}N(r)dr\right]\ , \qquad (5.5)$$

which clearly isolates the hard-core contribution to the pressure.

We define the local pressure $p(x)=s(x)/\beta$ as follows

$$s(x)=\rho(x)+\int_{x-a}^{x}dy\,[N_2(y|a)-\beta\int_{a+}^{\infty}\frac{\partial\varphi}{\partial r}N_2(y|r)dr]-\beta\theta(x-a)\int_0^{x-a}dy\int_{x-y}^{\infty}\frac{\partial\varphi}{\partial r}N_2(y|r)dr\ . \qquad (5.6)$$

The first term represents the kinetic momentum transfer per unit time from the left-hand side to the right-hand side of x. The term proportional to $N_2(y|a)$ accounts for the average momentum transfer due to hard collisions between the first particle on the left-hand side of x and the first particle on the right. The additional terms represent the average force between these particles due to the remainder of the interaction. The expression (5.6) corresponds precisely to the definition of the local pressure tensor given by Irving and Kirkwood[11] for the case of pair forces, when due account is taken of the hard core. They have shown that in the nonequilibrium case their definition leads to a local balance equation for the momentum density. In particular, it follows that in thermal equilibrium the equation of hydrostatic equilibrium is satisfied on the microscopic level.

It is easily shown, by taking the limit $x\to\infty$ in (5.6) and using (3.23), that in the bulk $s(x)$ tends to its bulk value s as given by the virial theorem (5.2). In order to show that in fact $s(x)=s$ for all x, we take Laplace transforms in (5.6). Using (3.23), (5.4), and the convolution theorem for Laplace integrals, one finds

$$\tilde{s}(\xi)=\tilde{\rho}(\xi)\,[1+s\,\frac{1-e^{-\xi a}}{\xi}-\beta\int_a^{\infty}dx\,e^{-\xi x}\int_x^{\infty}\frac{\partial\varphi}{\partial r}N(r)dr]\ , \qquad (5.7)$$

where the three terms correspond to the terms in (5.6). After some partial integrations and use of (3.13) this yields $\tilde{s}(\xi)=s/\xi$, which proves our statement.

We may remark at this point that several authors[12, 13] have given a rather involved definition of a local pressure $\hat{p}(x;L)$, in terms of the density profile $\rho(x;L)$, chosen in such a way that it satisfies

$$\ln\Xi(z,\beta,L)=\int_0^L\beta\hat{p}(x;z,\beta,L)dx\ . \qquad (5.8)$$

The spatial variation of the local pressure $\hat{p}(x;z,\beta,L)$ is such that one precisely recovers the surface and higher-order terms in (2.14). The definition (5.6) seems more natural; the absence of pressure gradients is also gratifying from a hydrodynamic point of view.

An additional argument in favor of the definition (5.6) is that the statement $s(x)=s$ may be viewed as an integrated form of the first equation of the equilibrium Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy. Integrating the Liouville equation over the coordinates and momenta of all but the ith particle, multiplying by the momentum of particle i and integrating over momentum, one finds in the thermodynamic limit

$$\frac{\partial P_i(x)}{\partial x}+\beta\left(\int_{x+a+}^{\infty}\frac{\partial\varphi(y-x)}{\partial x}P_{i,i+1}(x,y)dy+\int_0^{x-a+}\frac{\partial\varphi(x-y)}{\partial x}P_{i-1,i}(y,x)dy\right)+P_{i,i+1}(x,x+a)-P_{i-1,i}(x-a,x)=0\ , \qquad (5.9)$$

where we have adopted the convention $P_{0,1}=0$. Summing over i, one finds

$$\frac{\partial\rho(x)}{\partial x}+\beta\left(\int_{x+a+}^{\infty}\frac{\partial\varphi(y-x)}{\partial x}N_2(x|y-x)dy+\int_0^{x-a+}\frac{\partial\varphi(x-y)}{\partial x}N_2(y|x-y)dy\right)+N_2(x|a)-N_2(x-a|a)=0\ . \qquad (5.10)$$

In the case of pair forces, $N_2(x|r)$ may be replaced by $\rho_2(x|r)$ and in that case (5.10) becomes the BBGKY equation in its usual form. On differentiating (5.6) with respect to x and using (3.23), one finds that the result is identical with (5.10). Note that for the above argument it is not essential to take the thermodynamic limit. We could also have derived the equivalent form of (5.10) for the finite system and again have viewed the equation as the statement that the pressure is constant throughout the system.

Lebowitz and Percus[13] have derived a local compressibility theorem, which in the thermodynamic limit reads

$$\int_0^\infty [\rho_2(x,y)-\rho(x)\rho(y)]dy=\rho\left(\frac{\partial\rho(x)}{\partial s}\right)_\beta-\rho(x) \ . \qquad (5.11)$$

We may verify explicitly that this theorem is satisfied. From (3.18), we have

$$\begin{aligned}\int_0^\infty &[\rho_2(x,y)-\rho(x)\rho(y)]dy\\ &=\int_0^x [\rho(y)\rho g(x-y)-\rho(x)\rho(y)]dy\\ &\quad+\int_x^\infty [\rho(x)\rho g(y-x)-\rho(x)\rho(y)]dy\\ &=\int_0^\infty \rho(y)\rho g(x-y)dy-x\rho(x)\rho\\ &\quad+\rho(x)\int_0^\infty \rho G(r)dr-\rho(x)\Gamma \ . \qquad (5.12)\end{aligned}$$

Taking Laplace transforms and comparing the result with the transform of the right-hand side of (5.11) as given by (3.13), one finds that the (5.11) is indeed satisfied.

VI. POTENTIAL STEP

The analysis may be extended to the case where the system is bounded by hard walls at $x=-L'$ and $x=L$ with a finite potential of constant height Φ along the interval $(-L',0)$ (see Fig. 1). We number the particles along the line as follows

$$-L'<r_{N'}\leq,\ldots,\leq r_{1'}\leq 0\leq r_1\leq,\ldots,\leq r_N<L \ . \qquad (6.1)$$

The total interaction potential $U_{N+N'}$ for $N+N'$ particles is again assumed to be a sum of nearest-neighbor interactions. The potential Φ is equivalent to an activity z' to the left of the origin given by

$$z'=z\exp(-\beta\Phi) \ . \qquad (6.2)$$

Correspondingly the bulk density ρ' and bulk pressure p' on the left differ from the bulk values ρ and p on the right. The grand canonical partition function of the total system is given by

$$\Xi(z,z',\beta,L,L')=\sum_{N=0}^\infty\sum_{N'=0}^\infty z^N z'^{N'}\int_{-L'}^0\int_{r_{N'}}^0\cdots\int_{r_{N-1}}^L \exp(-\beta U_{N+N'})dr_{N'}dr_{N'-1},\ldots,dr_N \ . \qquad (6.3)$$

The Laplace transform with respect to L and L', defined by

$$\Psi(z,z',\beta,s,s')=\int_0^\infty dLe^{-sL}\int_0^\infty dL'e^{-s'L'}\Xi(z,z',\beta,L,L') \ , \qquad (6.4)$$

is found to be given by

$$\begin{aligned}\Psi(z,z',\beta,s,s')=&\frac{-1}{ss'}\,\frac{z'}{1-z'J(\beta,s')}\,\frac{J(\beta,s)-J(\beta,s')}{s-s'}\,\frac{z}{1-zJ(\beta,s)}\\ &+\frac{1}{ss'}+\frac{1}{s's^2}\,\frac{z}{1-zJ(\beta,s)}+\frac{1}{ss'^2}\,\frac{z'}{1-z'J(\beta,s')} \ , \qquad (6.5)\end{aligned}$$

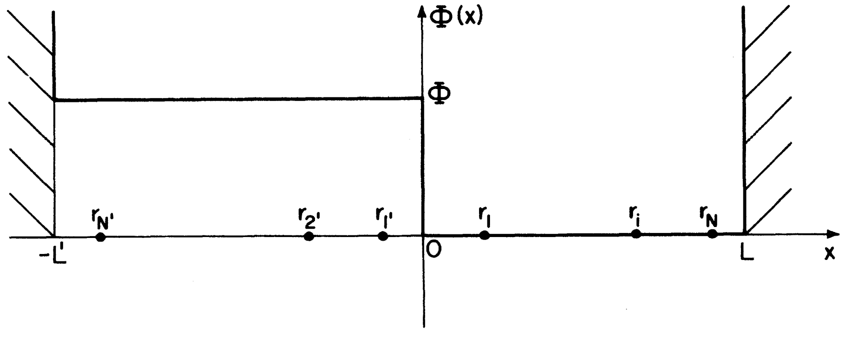

FIG. 1. A one-dimensional gas of particles in the presence of a potential step.

where we have made use of the general formula

$$\int_0^\infty dL e^{-sL} \int_0^\infty dL' e^{-s'L'} \int_0^L dx \int_{-L'}^0 dy f(x-y) = \frac{-1}{ss'} \frac{\tilde{f}(s) - \tilde{f}(s')}{s-s'} \quad . \tag{6.6}$$

Inverting the Laplace transform (6.5) one finds that the dominant contribution for large L and L' is given by the roots with largest real part s_0 and s_0' of $1 = zJ(\beta, s)$ and $1 = z'J(\beta, s')$, respectively. Thus, one has

$$\Xi(z, z', \beta, L, L')$$
$$= \frac{-1}{s_0 s_0'} \frac{1}{J_{;s}(\beta, s_0) J_{;s}(\beta, s_0')} \frac{J(\beta, s_0) - J(\beta, s_0')}{s_0 - s_0'} e^{s_0 L + s_0' L'} [1 + o(e^{-\lambda L}) + o(e^{-\lambda' L'})] \quad . \tag{6.7}$$

We shall again drop the subscript zero. The grand potential is given by (in obvious notation)

$$q(z, z', \beta, L, L') = sL + s'L' + \ln\left(\frac{-1}{ss'} \frac{1}{J_{;s} J'_{;s}} \frac{J-J'}{s-s'}\right) + o(e^{-\lambda L}, e^{-\lambda' L'}) \quad . \tag{6.8}$$

Subtracting the surface contributions from the two ends we therefore have for the interaction grand potential across the step

$$\omega(z, z', \beta) = \ln\left(\frac{-1}{ss'} \frac{1}{J_{;s} J'_{;s}} \frac{J-J'}{s-s'}\right) - \tfrac{1}{2}\psi(z, \beta) - \tfrac{1}{2}\psi(z', \beta) = \tfrac{1}{2} \ln\left[\frac{1}{J_{;s} J'_{;s}} \left(\frac{J-J'}{s-s'}\right)^2\right], \tag{6.9}$$

where we have made use of (2.17).

The probability density for finding the first particle on the left of the origin at x' and the first particle on the right at x is given by

$$P_{1',1}(x', x; L, L') = z'z \frac{\Xi^0(z', \beta, L' + x') \Xi^0(z, \beta, L - x)}{\Xi(z, z', \beta, L, L')} \exp[-\beta\varphi(x - x')] \quad . \tag{6.10}$$

Hence, we obtain in the thermodynamic limit $L, L' \to \infty$

$$P_{1',1}(x', x) = -\frac{s-s'}{J-J'} e^{s'x' - sx - \beta\varphi(x-x')} \quad . \tag{6.11}$$

All the other distribution functions may be found by convoluting this distribution with the nearest-neighbor distribution $N(r) \equiv N(r; z, \beta)$ on the right-hand side and with the distribution $N'(-r) \equiv N(-r; z', \beta)$ on the left-hand side. We need to carry out this procedure only on one side explicitly. The Laplace transform of the distribution $P_{1',1}(x',x)$ is given by

$$\tilde{P}_{1',1}(\eta, \xi) = \int_{-\infty}^0 dx' e^{\eta x'} \int_0^\infty dx e^{-\xi x} P_{1',1}(x', x)$$
$$= \frac{s-s'}{J-J'} \frac{J[\xi] - J'[\eta]}{s + \xi - s' - \eta} \quad . \tag{6.12}$$

Hence, we have for the transform of $P_i(x)$

$$\tilde{P}_i(\xi) = \frac{s-s'}{J-J'} \frac{J[\xi] - J'}{s + \xi - s'} \left(\frac{1}{1 - zJ[\xi]}\right)^{i-1} \quad . \tag{6.13}$$

The Laplace transform of the density profile $\rho(x)$ is therefore

$$\tilde{\rho}(\xi) = \frac{s-s'}{J-J'} \frac{J[\xi] - J'}{s + \xi - s'} \left(\frac{1}{1 - zJ[\xi]}\right) \cdot \tag{6.14}$$

Again there is a simple relationship with the bulk pair correlation function, namely for $x > 0$

$$\rho(x) = \rho + (s - s')e^{-(s-s')x} \left(\frac{z}{z-z'} - \frac{\rho}{s-s'} + \int_0^x \rho G(r) e^{(s-s')r} dr\right) . \tag{6.15}$$

In the limit of an infinitely high step on the left-hand side, z' and s' tend to zero and we recover the result (3.20). The particle excess may be found as before and is given by[13]

$$\Gamma_0 = \int_0^\infty [\rho(x) - \rho] dx$$
$$= \frac{1}{2}\left(\frac{\partial \rho}{\partial s}\right)_\beta + \tfrac{1}{2} - \frac{\rho}{s-s'} + \frac{z'}{z-z'} , \tag{6.16}$$

where we have used a subscript zero to distinguish Γ_0 from Γ of Sec. IV. From (6.15), it follows that the density at the step is given by

$$\rho(0+) = z \frac{s-s'}{z-z'} \quad . \tag{6.17}$$

Hence there is a density discontinuity

$$\rho(0+) - \rho(0-) = s - s' . \tag{6.18}$$

It is interesting to compare the result (6.15) with that obtained by applying linear response theory. To first order the response of the uniform system to an external potential $\Phi(x)$ is given by[13]

$$\delta\rho(x) = -\beta \int_{-\infty}^{0} [\rho\delta(x-y) + \rho^2 G(x-y)]\Phi(y)dy . \tag{6.19}$$

Hence, for the potential step we have (for $x > 0$)

$$\delta\rho(x) = -\beta\Phi \int_{-\infty}^{0} \rho^2 G(x-y)dy$$
$$= \beta\Phi\left[-\tfrac{1}{2} z^2 \left(\frac{\partial^2 s}{\partial z^2}\right)_\beta + \int_0^x \rho^2 G(r)dr\right], \tag{6.20}$$

which may be checked to be in agreement with (6.15).

For the pair distribution in the thermodynamic limit as defined by (3.16), we find as before for $x > 0$, $r > 0$

$$\rho_2(x|r) = \rho(x)\rho g(r) , \tag{6.21}$$

where now $\rho(x)$ is given by (6.15). For $x < 0$, $r < 0$, a similar expression holds in the primed quantities. The neighbor pair distribution for $x > 0$, $r > 0$ is given by

$$N_2(x|r) = \rho(x)N(r) . \tag{6.22}$$

Hence, we may calculate the surface energy across the step, defined by

$$\begin{aligned}\mathcal{E}_0(z, z', \beta) = {} & \tfrac{1}{2} k_B T(\Gamma_0 + \Gamma_0') + 2\Delta_0(z, z', \beta) \\ & + \int_0^\infty dx \int_0^\infty dr\varphi(r)[N_2(x|r) - \rho N(r)] \\ & - \Delta(z, \beta) + \int_{-\infty}^0 dx' \int_0^\infty dr\varphi(r)[N_2'(x'| \\ & - r) - \rho' N'(r)] - \Delta(z', \beta) ,\end{aligned} \tag{6.23}$$

where

$$2\Delta_0(z, z', \beta) = \int_{-\infty}^0 dx' \int_0^\infty dx\varphi(x - x')P'_{1',1}(x', x) \tag{6.24}$$

is the interaction energy across the step. Using (6.11), one finds

$$2\Delta_0 = -\frac{J_{;\beta} - J'_{;\beta}}{J - J'} = \frac{z\langle\varphi\rangle' - z'\langle\varphi\rangle}{z - z'} . \tag{6.25}$$

From (6.22) and (6.23), we find for the surface energy

$$\begin{aligned}\mathcal{E}_0(z, z', \beta) = {} & \tfrac{1}{2} k_B T(\Gamma_0 + \Gamma_0') + \Gamma_0\langle\varphi\rangle - \Delta \\ & + \Gamma_0'\langle\varphi\rangle' - \Delta' + 2\Delta_0 .\end{aligned} \tag{6.26}$$

The interaction grand potential (6.9) may again be expressed in terms of bulk thermodynamic properties, namely,

$$\omega(z, z', \beta) = \tfrac{1}{2} \ln\left[\frac{\rho\rho'}{zz'}\left(\frac{z - z'}{s - s'}\right)^2\right] . \tag{6.27}$$

Hence, one finds by differentiation and use of (6.16)

$$\left(\frac{\partial\omega}{\partial z}\right)_{z', \beta} = \frac{\Gamma_0}{z} . \tag{6.28}$$

Similarly, one obtains, with the aid of (2.16), (4.23), (6.16), and (6.25),

$$-\left(\frac{\partial\omega}{\partial\beta}\right)_{z, z'} = \Gamma_0\langle\varphi\rangle - \Delta + \Gamma_0'\langle\varphi\rangle' - \Delta' + 2\Delta_0 . \tag{6.29}$$

Hence, we may write

$$d\omega = \Gamma_0 d\ln z + \Gamma_0' d\ln z' - U_\Phi d\beta , \tag{6.30}$$

where U_Φ is the surface potential energy given by (6.29). As the potential step decreases to zero, the defects cancel against the interaction energy across the step. The total energy thus tends to the correct bulk value plus the surface contributions from the two ends of the system.

Finally, we may again define a local pressure $p(x)$. For $x > 0$, the definition is identical to (5.6) except for additional terms linear in $P'_{1',1}(x', x)$, accounting for the force exerted by particle 1′ on particle 1. By a rather elaborate calculation one may again show that for $x > 0$ the pressure is constant, $p(x) = p$. Similarly one has $p(x') = p'$ for $x' < 0$. Hence, there is hydrostatic equilibrium throughout the system in the sense

$$s(x) = s_0(\beta, z\exp[-\beta\Phi(x)]), \quad -\infty < x < +\infty , \tag{6.31}$$

where $\Phi(x) = \Phi\theta(-x)$. The BBGKY equation (5.10) is easily extended to account for an arbitrary external potential $\Phi(x)$, so that one may conclude that Eq. (6.31) holds generally. Alternatively this follows from an analysis similar to that given by Irving and Kirkwood.[11] It is interesting to note from (6.18) that the pressure discontinuity $p(0+) - p(0-)$ at $x = 0$ still has an ideal gas character in spite of the fact that $\beta p(0\pm) \neq \rho(0\pm)$. Presumably this is a general feature reflecting the fact that the discontinuity in the distribution functions does not give rise to a discontinuity in the interaction contribution to the local pressure, which involves an integral over distribution functions.

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