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A LOWER BOUND TO THE PRESSURE IN ONE-DIMENSIONAL SYSTEMS

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Davis, California

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ABSTRACT

Using a minimum principle for the grand potential a lower bound is derived for the pressure of a one-dimensional gas as a function of temperature and chemical potential.

In this paper we derive a lower bound for the pressure of a one-dimensional system at fixed temperature, volume and chemical potential. We do this by using the well-known variational principle which states that the minimum value of the grand potential defined by:

$$I(T, V, \mu) = E - \mu N - TS = -pV \quad (1)$$

where E is the ensemble average of the Hamiltonian and S is the ensemble entropy, is obtained by choosing the equilibrium ensemble:

$$P_N(x_1, \dots, x_N, p_1, \dots, p_N) = C \exp \beta(\mu N - H_N(x, p)). \quad (2)$$

Let us first define E , N , and S in more detail. We represent a grand ensemble by a sequence of probability functions P_N such that the probability of finding exactly N particles in the system and further finding them, (in any order) in the neighborhoods of the phase space points x_j, p_j is given by:

$$P_N(x_1, \dots, x_N, p_1, \dots, p_N) dx_1 \dots dx_N dp_1 \dots dp_N. \quad (3)$$

If we now sum over all physically distinct possibilities we must obtain one.

$$\sum_N \int_{0 < x_1 < \dots < x_N < L} dx_1 \dots dx_N \int_{-\infty}^{\infty} dp_1 \dots dp_N P_N(x, p) = 1. \quad (4)$$

Let us denote the N -dimensional region $0 < x_1 < \dots < x_N < L$ as Ω_N . The energy, average number of particles, and entropy are defined by:

$$E = \sum_N \int_{\Omega_N} d^N x \int_{-\infty}^{\infty} d^N p H_N(x, p) P_N(x, p), \quad (5)$$

$$N_0 = \sum_N N \int_{\Omega_N} d^N x \int_{-\infty}^{\infty} d^N p P_N(x, p), \quad (6)$$

and

$$S = k \sum_N \int_{\Omega_N} d^N x \int_{-\infty}^{\infty} d^N p P_N(x, p) \ln P_N(x, p). \quad (7)$$

We shall assume that the Hamiltonian is of the usual form:

$$H_N(x, p) = \sum_{j=1}^N \frac{p_j^2}{2m} + \sum_{i < j} V(x_i - x_j). \quad (8)$$

For the equilibrium ensemble one can almost never do the integrations necessary to calculate I as a function of μ , V , and T . We shall describe a certain class of ensembles for which all the necessary integrals may be evaluated. The minimum value of I within this class of ensembles is then larger than the value of I given by the equilibrium ensemble. The pressure associated with this ensemble is thus less than or equal to the equilibrium pressure. Since the momentum integrations in the equilibrium ensemble are trivial we shall assume that all our ensembles have Maxwell distribution in momenta and discuss only the configuration integrals. We construct our ensembles as follows. We begin with a large collection of empty semi-infinite line segments. $(0, \infty)$. We distribute one particle on each line segments such that the probability that it is between x and $x+dx$ is $F(x)dx$. Clearly

$$F(x) \geq 0 \quad (9)$$

and:

$$\int_0^{\infty} F(x) dx = 1. \quad (10)$$

We now place a second particle on each line segment, always to the right of the first, such that the probability that the second particle is a distance x from the first is $F(x)dx$. We continue this process with a third particle, a fourth, and so on to infinity.

What is then the probability that the line segment $0 < x < L$ contains exactly N particles at positions $x_1, \dots, x_N$? We assume $0 < x_1 < \dots < x_N < L$. This is just the probability that the first N particles are at $x_1, \dots, x_N$ while the $(N+1)$ th particle has any coordinate larger than L . This is, by our construction equal to:

$$P_N(x_1, \dots, x_N) = F(x_1) F(x_2 - x_1) \dots F(x_N - x_{N-1}) \int_L^\infty f(y - x_N) dy. \quad (11)$$

To see how one evaluates the multidimensional integrals with this ensemble let us verify that the above probability distributions are correctly normalized; a fact which is not obvious from their form. We thus want to calculate the sum:

$$J(L) = P_0 + \sum_{N=1}^{\infty} \int_{\Omega_N} P_N(x_1, \dots, x_N) dx_1 \dots dx_N. \quad (12)$$

If we define a function $f(x)$ by:

$$f(x) = \int_x^\infty F(y) dy \quad (13)$$

and we use the following symbol for the convolution integral:

$$\phi_1 * \phi_2 * \dots * \phi_N(x_N) \equiv \int_{0 < x_1 < \dots < x_N} \phi_1(x_1) \phi_2(x_2 - x_1) \dots \phi_N(x_N - x_{N-1}) dx_1 \dots dx_{N-1} \quad (14)$$

then it is easy to see that J is given by:

$$J(L) = f(L) + F*f(L) + F*F*f(L) + \dots \quad (15)$$

Now we use the fact that the Laplace transform of a convolution of functions is simply the product of the Laplace transforms of the functions. Thus

if:

$$\tilde{J}(s) = \int_0^{\infty} e^{-sL} J(L) dL, \quad (16)$$

$$\tilde{F}(s) = \int_0^{\infty} e^{-sx} F(x) dx, \quad (17)$$

and:

$$\tilde{f}(s) = \int_0^{\infty} e^{-sx} f(x) dx \quad (18)$$

then:

$$\tilde{J}(s) = \tilde{f}(s) + \tilde{F}(s) \tilde{f}(s) + \tilde{F}^2(s) \tilde{f}(s) + \dots$$

$$= \frac{\tilde{f}(s)}{1 - \tilde{F}(s)}. \quad (19)$$

If we use the definition of $f(x)$ (Equation 13) and the facts that $f'(x) = -F(x)$ and $f(0) = 1$ we can, by a partial integration express $\tilde{f}(s)$ in terms of $\tilde{F}(s)$.

$$\begin{aligned} \tilde{f}(s) &= \int_0^{\infty} e^{-sx} f(x) dx = \left[s^{-1} e^{-sx} F(x) \right]_0^{\infty} - s^{-1} \int_0^{\infty} e^{-sx} F(x) dx \\ &= s^{-1} \left(1 - \tilde{F}(s) \right). \end{aligned} \quad (20)$$

Thus using the inverse Laplace transform to evaluate $J(L)$ we find, as expected, that:

$$J(L) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} J(s) e^{sL} ds = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} e^{sL} \frac{ds}{s} = 1. \quad (21)$$

Using similar techniques we shall now calculate all those quantities needed to evaluate the grand potential in terms of $\tilde{F}(s)$.

1. The one-particle density

$$\begin{aligned} \rho_1 &= \sum_{N=1}^{\infty} \left(\frac{N}{L}\right) \int_{\Omega_N} P_N(x_1, \dots, x_N) d^N x = \\ &= \sum \left(\frac{N}{L}\right) \int_{\Omega_N} F(x_1) F(x_2 - x_1) \dots F(x_N - x_{N-1}) f(L - x_N) d^N x. \end{aligned} \quad (22)$$

The Laplace transform of ρ_1 is given by:

$$\begin{aligned} \tilde{\rho}_1(s) &= \int_0^{\infty} \rho_1(L) e^{-Ls} dL = \\ &= \sum \left(\frac{N}{L}\right) (\tilde{F}(s))^N \tilde{f}(s) \\ &= L^{-1} \frac{\tilde{F}(s)}{s(1 - \tilde{F}(s))} = L^{-1} \left\{ \frac{1}{s(1 - \tilde{F})} - \frac{1}{s} \right\} \end{aligned} \quad (23)$$

$$\rho_1 = \frac{1}{2\pi i} \int_B e^{Ls} \tilde{\rho}_1(s) ds \quad (24)$$

where the symbol $\int_B$ denotes the Bromwich integral $\int_{c-i\infty}^{c+i\infty}$

It is easy to prove that $|\tilde{F}(s)| > 1$ for $\text{Re}(s) \geq 0$ except at $s = 0$ where $F(s) = 1$. Thus $(1 - \tilde{F}(s))^{-1}$ has singularities only at zero and in the left half plane. The singularities in the left half plane may be neglected since the exponential e^{Ls} would make the residue exponentially small for large L . The only non-negligible contribution is:

$$\rho_1 = - \left(\frac{d\tilde{F}(s)}{ds} \right)_{s=0}^{-1} \quad (25)$$

The above result becomes transparent if we notice that

$$\left(\frac{d\tilde{F}(s)}{ds} \right)_{s=0} = - \int_0^{\infty} x F(x) dx \quad (26)$$

which is simply the average distance between neighboring particles.

2. The two-particle density.

We shall normalize the two particle density so that:

$$\int_0^L dx_2 \int_0^{x_2} dx_1 \rho_2(x_2 - x_1) = N(N-1)/2 \quad (27)$$

which is equivalent to saying that $\rho_2(x_2 - x_1) dx_1 dx_2$ is the probability of simultaneously finding a particle in the interval dx_1 and another in the interval dx_2 . This probability can be expressed as the product of the probability of finding a particle in dx_1 and the conditional probability of finding a particle in dx_2 if one is known to be in dx_1 . The first factor is simply $\rho_1 dx_1$ while the second factor is given by the series:

$$F(x_{12}) + F*F(x_{12}) + F*F*F(x_{12}) + \dots \quad (28)$$

$$\text{where } x_{12} = x_2 - x_1.$$

The reader can convince himself that the series expansion is correct by remembering that, due to the way the ensemble was constructed, if there is a particle at x_1 the probability that its nearest neighbor is at x_2 is $F(x_{12})$. The second term in the series is simply the probability that the next nearest neighbor is at x_2 and so forth. Thus the two-particle density is:

$$\rho_2(x_{12}) = \rho_1(F(x_{12}) + F*F(x_{12}) + F*F*F(x_{12}) + \dots). \quad (29)$$

The Laplace transform of ρ_2 is:

$$\begin{aligned} \tilde{\rho}_2(s) &= \rho_1(\tilde{F}(s) + \tilde{F}^2(s) + \dots) \\ &= \frac{\rho_1 \tilde{F}(s)}{1 - \tilde{F}(s)}. \end{aligned} \quad (30)$$

3. The potential energy.

The ensemble average of the potential energy is:

$$\begin{aligned} V(L) &= \int_0^L dx_1 \int_{x_1}^L dx_2 v(x_2 - x_1) \rho_2(x_2 - x_1) \\ &\approx L \int_0^\infty dx v(x) \rho_2(x) \\ &= \frac{L}{2\pi i} \int_B \tilde{V}(-s) \tilde{\rho}_2(s) ds \end{aligned}$$

$$= \frac{N_0}{2\pi i} \int_B \frac{V(-s)F(s)}{1 - \tilde{F}(s)} ds \quad (31)$$

where $N_0 = \rho_1 L$

4. The configuration entropy.

The configuration entropy is:

$$S = -k \int_{\Omega_N} P_N(x_1, \dots, x_N) \ln P_N(x_1, \dots, x_N) d^N x. \quad (32)$$

A straightforward calculation shows that

$$S = \frac{1}{2\pi i} \int_B e^{Ls} \tilde{S}(s) ds \quad (33)$$

where:

$$S(s) = \frac{k G(s)}{s(1 - F(s))}.$$

and:

$$G(s) = - \int_0^\infty e^{-sx} F(x) \ln F(x) dx. \quad (34)$$

Once again the only important contribution to the integral is from the singularity at $s = 0$. Thus:

$$S = -k N_0 \int_0^\infty F(x) \ln F(x) dx. \quad (35)$$

In order to evaluate the pressure associated with our ensemble we collect our formulas for V , ρ_1 , and S and add to them the contribution to the grand potential of the momentum degrees-of-freedom. The result is:

$$-pV = I = N_o \left(\frac{1}{2} kT + \frac{1}{2\pi i} \int_B \frac{\tilde{v}(-s) \tilde{F}(s)}{1 - \tilde{F}(s)} ds - \mu + kT \int_0^\infty F(x) \ln F(x) dx \right) \quad (36)$$