

## Distribution Functions and Thermodynamic Functions of Many Particle Systems\*

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A method is given of determining an upper bound of the entropy of a classical interacting system. If the distribution function can be split into an interaction part and a free particle part, then the former plays the role of reducing the entropy. When a Gaussian type distribution function can be introduced for the first trial description of the spatial distribution, the next distribution function can be obtained by a product of the Gaussian function and the Boltzmann factor. A family of Gaussian trial distribution functions is introduced for an electron gas. It was found that the ring diagram energy corresponds to the minimum free energy which the family produces. In contrast to the ring diagram method, our new approach is extremely simple and general.

Apresenta-se um método de determinação de um limite superior para a entropia de sistemas de muitos corpos em interação. Caso a função de distribuição possa ser dividida em parte de interação e em outra de partículas livres, a primeira traz consigo a redução da entropia. Quando uma função de distribuição, de forma gaussiana puder ser introduzida, na tentativa inicial de descrição da distribuição espacial, a função de distribuição seguinte poderá ser obtida por produto da função gaussiana pelo fator de Boltzmann. Neste trabalho, apresenta-se uma família de gaus-

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sianas tentativas para um gas de electrons. Achou-se que o diagrama em anel, para a energia, corresponde ao menor valor da energia a que a família dá lugar. Contrastando com o método dos diagramas em anel, a abordagem nova, a ser exibida, é extremamente simples e geral.

## 1. INTRODUCTION

The entropy of a physical system is defined, in statistical mechanics, either by the Boltzmann relation<sup>1</sup>

$$S = \kappa \ln W, \quad (1.1)$$

or by the H function<sup>2</sup>

$$S = -\kappa \int f(x) \ln f(x) dx. \quad (1.2)$$

Here,  $W$  is the number of possible configurations, and  $f(x)$  is the distribution function of the system,  $x$  being a symbolic phase space variable.

Equations (1.1) and (1.2) are equivalent. In using these relations, a maximization process is commonly used for establishing equilibrium. Through this maximization of the entropy,  $W$  or  $f(x)$  for equilibrium are determined. The Gibbs H-theorem for the canonical distribution function is based on a maximum entropy.

The configurational function,  $W$ , or the distribution function  $f(x)$ , includes, generally, parameters characterizing the system and some adjustable parameters which can be used for maximization. For instance, the normalization condition of the distribution function introduces an adjustable parameter when Lagrange's method of multipliers is used.

It is clear that the absolute magnitude of the entropy determined by Eq. (1.2) depends on how the distribution function is normalized. Since, in most cases, only the relative entropy changes are important, the ambiguity in normalization is generally irrelevant. However, there are also cases where the absolute magnitude of the entropy becomes important.

The third law of thermodynamics is a typical example.

It is the purpose of this paper to discuss some very general aspects of the entropy which are important for arbitrary interacting systems. In the first place, we shall show that the entropy has an upper bound which is proportional to the total number of constituents,  $N$ , of the system. Hence, the existence of the thermodynamic limit will be clear if a lower bound is found also proportional to the total number. We shall then analyse the role played by molecular interactions. In a subsequent paper, we shall show how the general consideration in the present paper is applicable to many body systems for explicit results. In fact, significant and explicit results shall be derived for typical many body systems. For convenience, in the present paper, we shall assume the system to be classical. Otherwise, our considerations will be completely general. Although we do not introduce time explicitly, our consideration will be valid even if the system is in non-equilibrium.

## 2. UPPER BOUND FOR THE ENTROPY

For our purpose of finding an upper bound for the entropy, let us use the inequality

$$\int f(x) \ln f(x) dx \geq \int f(x) \ln g(x) dx, \quad (2.1)$$

where

$$\int f(x) dx = \int g(x) dx. \quad (2.2)$$

This inequality holds for arbitrary non negative distribution functions,  $f(x)$  and  $g(x)$ , satisfying the same normalization, i.e. (2.2). The proof of the inequality has been given elsewhere<sup>3</sup> but since it does not take space, we give an outline of it:

$$\int \{f(x) \ln f(x) - f(x) \ln g(x)\} dx = \int g(x) \left\{ \frac{f(x)}{g(x)} \ln \frac{f(x)}{g(x)} - \frac{f(x)}{g(x)} + 1 \right\} dx \geq 0 \quad (2.3)$$

Here, in the second equation, the important condition (2.2) has been introduced, and the non negative character of the integrand used.

In the distribution function, we have used a symbolic variable  $x$ .

This variable can represent velocities, coordinates and even discrete variables (such as spins).

A set of conjugate phase space variables may have a dimension, but the form of Eq. (1.2) suggests that intrinsic properties of the entropy can be studied by using dimensionless phase space variables,  $x$ , and a dimensionless  $f(x)$ , because the dimension of the entropy has been provided by the Boltzmann constant  $\kappa$ .

Based on this observation, let us consider a three-dimensional system which is described by a "true" distribution function,  $f(x)$ . Let us assume that  $f(x)$  is unknown but a trial distribution function  $g(x)$  exists. Let us choose

$$g(x) = \left(\frac{\lambda}{\pi}\right)^{3/2} \exp(-\lambda x^2) , \quad (2.4)$$

which is normalized to 1 in the 3-D space and has an adjustable parameter. Obviously,  $g(x)$  represents the Maxwell distribution function if  $x^2 = mv^2/2\kappa T$ . Introducing Eq. (2.4) into ineq. (2.1), we find

$$\frac{S}{\kappa} \leq \lambda \langle x^2 \rangle + \frac{3}{2} \ln \frac{\pi}{\lambda} , \quad (2.5)$$

where  $\langle x^2 \rangle$  is the second moment of  $f(x)$ . Since  $f(x)$  is normalized to 1, as  $g(x)$  is,

$$\langle x^2 \rangle = \int x^2 f(x) dx . \quad (2.6)$$

The parameter  $\lambda$  can be chosen such that the right hand side is a minimum. Then

$$\frac{S}{\kappa} \leq \frac{3}{2} \left[ 1 - \ln \frac{3}{2\pi \langle x^2 \rangle} \right] , \quad \lambda = \frac{3}{2} \langle x^2 \rangle^{-1} . \quad (2.7a)$$

It is interesting to observe, in ineq. (2.5), that the second moment of the distribution function determines the upper bound. Note that the sharper the distribution, the smaller the upper bound.

We have used a single variable,  $x$ , in Eq.(2.4). It is straightforward to generalize the above considerations to the case of  $N$  particles. If these particles are the same, we will have

$$\frac{S}{k} \leq \frac{3N}{2} \left[ 1 - \ln \frac{3}{2\pi \langle x^2 \rangle} \right] . \quad (2.7b)$$

Hence, the entropy of the system can be proportional to  $N$  if a lower bound for the entropy  $S$  is proportional to  $N$ . We would then establish the existence of the thermodynamic limit.

### 3. INTERACTION EFFECT

Let us investigate the case where the phase space is characterized by two variables  $p$  and  $q$ . Let us associate  $p$  with momentum space, and  $q$  with coordinate space. If the system is classical, we can express the "true" distribution function  $f(p,q)$  in a product form:

$$f(p,q) = f_1(p) f_2(q) , \quad (3.1)$$

where  $f_1(p)$  shall be the Maxwell distribution in momentum space, as in Eq. (2.4), and  $f_2(q)$  represents the coordinate space part. Let us use the normalization:

$$\int f(p,q) dp dq = \int f_1(p) dp \int f_2(q) dq = \int f_2(q) dq = 1. \quad (3.2)$$

Correspondingly, we choose a "trial" distribution, in the  $p$ - $q$  space, as follows

$$g(p,q) = f_1(p) \times 1 . \quad (3.3)$$

This "trial" distribution function is constant (white spectrum for our information) in coordinate space. Since  $g(p, q)$  has to be normalized as in Eq. (3.2), we require

$$\int dq = 1 . \quad (3.4)$$

That is,  $dq = d\vec{x}/V$ , where  $V$  is the total volume and  $d\vec{x}$  is the volume element.

Introducing Eqs. (3.1) and (3.3) into ineq. (2.1), we find

$$\int f_2(q) \ln f_2(q) dq \geq 0 . \quad (3.5)$$

Note that, with the product form of Eq. (3.1), the total entropy of the system is the sum of the momentum space part and the coordinate space part. Ineq. (3.5) states that the interaction part of the entropy is negative. That this is an intrinsic property of the entropy is clear because we have been using a dimensionless variable. Actually, the result (3.5) is a direct consequence of ineq. (2.1) when  $g(x)$  is set equal to 1. The physical meaning of this negativeness has yet to be explored. The result is quite general, being independent of the particular spatial distribution of the system and of the character of the potential, attractive or repulsive, which produces it.

The crucial point is that the interaction causes a certain spatial order which in turn results in an entropy reduction. From this viewpoint, interactions always feed negative values to the entropy.

We have considered rather simple cases where the trial distribution function,  $g(x)$ , does not depend on coordinates. Since it is often possible to describe a system approximately by an effective field, let us choose a "trial" distribution function such that

$$\begin{aligned} g^{(0)}(p, q) &= g_1^{(0)}(p) g_2^{(0)}(q) \\ &= \prod_{i=1}^N g_1^{(0)}(p_i) g_2^{(0)}(q_i) , \end{aligned} \quad (3.6)$$

where  $g_2^{(0)}(q_{ij})$  represents the part due to the effective field. It is a function of a single particle coordinate,  $q_i$ . The function  $g_1^{(0)}(p_i)$  represents the kinetic energy part. Eq. (3.6) improves Eq. (3.3). Again, to the true distribution function may be given the form of Eq. (3.1). More explicitly, we use

$$f(p, q) = \prod_{i=1}^N f_1(p_i) \prod_{(ij)} f_2(q_{ij}), \quad (3.7)$$

where  $q_{ij} = q_i - q_j$  and  $(ij)$  means a pair of particles,  $i$  and  $j$ . We have the normalization condition that

$$\begin{aligned} \int f(p, q) dp dq &= \int \prod_{(ij)} f_2(q_{ij}) \prod_{i=1}^N dq_i \\ &= \int \prod_{i=1}^N g_2^{(0)}(q_i) dq_i = Q_N = \exp(-\beta F), \quad (3.8) \end{aligned}$$

where  $F$  is the interaction part of the free energy,  $Q_N$  being the configurational partition function.

Under this condition, ineq. (2.1) becomes

$$\int \rho_2(q_{12}) \ln f_2(q_{12}) dq_1 dq_2 > \int \rho_1(q_1) \ln g_2^{(0)}(q_1) dq_1, \quad (3.9)$$

where  $\rho_2(q_{ij})$  and  $\rho_1(q_1)$  are the pair and singlet distribution functions of the given system:

$$\rho_2(q_{12}) = \frac{N(N-1)}{Q_N} \int \prod_{(ij)} f_2(q_{ij}) \prod_{i \neq 1, 2} dq_i, \quad (3.10)$$

$$\rho_1(q_1) = \frac{N}{Q_N} \int \prod_{(ij)} f_2(q_{ij}) \prod_{i \neq 1} dq_i.$$

The normalization of these functions are

$$\int \rho_2(q_{12}) dq_1 dq_2 = N(N-1), \quad \int \rho_1(q_1) dq_1 = N. \quad (3.11)$$

Inequality (3.9) then indicates that the true entropy, as given by the left hand side, has an upper bound. That is

$$SI < N\kappa < \ln g_2^{(0)}(q_1) > , \quad (3.12)$$

where  $\langle \ln g_2^{(0)}(q_1) \rangle$  indicates the average taken with respect to  $\rho_1(q_1)$ .

We conclude that the use of an effective field distribution function  $g_2^{(0)}(q_1)$  increases the entropy.

The formal aspects of the entropy, which we have discussed in the previous sections, do not change. Here  $S_I$  denotes the part of the entropy which depends on the interaction. Note that ineq. (3.12) can be much more restrictive than what ineq. (3.5) suggests: the average  $\langle \ln g_2^{(0)}(q_1) \rangle$  can be negative for  $g_2^{(0)}(q_1) = \exp[-\beta\phi(q_1)]$ , where  $\phi(q_1)$  is the effective potential and  $\beta = 1/\kappa T$ . So far, we have discussed some formal aspects of the entropy. It is very desirable to find a lower bound which is proportional to  $N$ . However, this may not be generally possible because the relevant states must be those where the interaction is effective. The specification of such states should vary from one system to another. In other words, it is difficult to specify a unique state which corresponds to minimum entropy.

Inequality (3.9) suggests that a suitable choice of  $g_2^{(0)}(q_1)$  should give a good approximation to the left hand side which is generally unknown. In practice, it is perhaps more convenient to express the inequality in terms of the free energy. If, as in Eq. (3.6), a trial distribution function is chosen, and if the next approximation is chosen such that

$$g^{(1)}(p, q) = g^{(0)}(p, q) \exp[\beta(F - \phi)] , \quad (3.13)$$

the Bogoliubov inequality will read

$$\langle \phi \rangle_0 \geq F , \quad (3.14)$$



where  $\langle \phi \rangle_0$  indicates the average taken with respect to  $g^{(0)}(p, q)$ . The free energy,  $F$ , can be found from the normalization condition

$$\int f(x) dx = 1, \tag{3.15}$$

or

$$\exp(-\beta F) = \langle \exp(-\beta \phi) \rangle_0. \tag{3.15}$$

As in the case of ineq. (3.9), we try to choose  $\langle \phi \rangle_0$  as low as possible so that a very good approximation for  $F$  is obtained. This depends on the choice of the trial distribution  $g^{(0)}(p, q)$ .

#### 4. APPLICATION TO THE ELECTRON GAS

Let us now apply our considerations of Section 3 to an electron gas. We will show that the ring diagram formula for a classical electron gas can be obtained very easily.

For an electron gas, with positive charges in the background, we require charge neutrality. Therefore, it is reasonable to choose  $g(x)$  in such a way that the left hand side of ineq. (3.14) does vanish. This means that  $g(x)$  should correspond to a completely random distribution without any effect from the Coulomb interaction.

We start with the momentum space representation of the Coulomb interaction:

$$H = \frac{1}{2V} \sum_{\vec{q} \neq 0} u(\vec{q}) \{ (\rho_{\vec{q}})^2 - N \}, \tag{4.1}$$

where

$$u(\vec{q}) = \frac{4\pi e^2}{q^2}, \quad \rho_{\vec{q}} = \sum_{i=1}^N \exp(i\vec{q} \cdot \vec{r}_i). \tag{4.2}$$

The sum for  $\rho_{\vec{q}}$  may be considered as a random process

Hence, by analogy to the case of an ideal gas, we choose the zeroth order "trial" distribution function, which serves actually as a weight function, as follows:

$$\int g^{(0)}(x) dx = c \int \exp(-2\lambda x^2) x^{2\lambda-1} dx, \quad (4.3)$$

where  $\lambda$  is an adjustable parameter,  $c$  the normalization constant, and

$$x = \frac{|\rho(\vec{q})|}{(2N)^{1/2}}. \quad (4.4)$$

The factor  $N^{1/2}$  keeps the magnitude of  $x$  small. The next order trial function is given the form of Eq. (3.13):

$$g^{(1)}(x) = g^{(0)}(x) \exp \beta \left[ F - \sum_{q \neq 0} nu(q) \left\{ x^2(\vec{q}) - \frac{1}{2} \right\} \right], \quad (4.5)$$

where  $n = NV$ .

Since  $g^{(0)}(x)$  and hence  $g^{(1)}(x)$  are normalized to one, we find

$$\exp(-\beta F) = \prod_{q \neq 0} \langle \exp\{-\beta nu(\vec{q}) [x^2(\vec{q}) - \frac{1}{2}]\} \rangle_0, \quad (4.6)$$

which corresponds to Eq. (3.15). With Eq. (4.3), the average can be taken at once. We arrive at

$$F = \frac{1}{2\beta} \sum_{q \neq 0} \left\{ \ln \left[ 1 + \frac{k^2}{2\lambda q^2} \right]^{2\lambda} - \frac{k^2}{q^2} \right\}, \quad (4.7)$$

where  $k$  is the Debye constant given by

$$k^2 = 4\pi\beta ne^2. \quad (4.8)$$

The free energy given by Eq. (4.7) depends on the parameter  $A$ . It is interesting to observe that, for large  $q$ , the first expansion term of the

logarithmic function is cancelled exactly by the second term, irrespective of  $\lambda$ . The free energy is lower for smaller  $\lambda$ , but since the form of Eq. (4.3) requires  $\lambda > 1/2$ , the lowest free energy expression is

$$F = \frac{1}{2\beta} \sum_{q \neq 0} \left\{ \ln \left[ 1 + \frac{k^2}{\vec{q}^2} \right] - \frac{k^2}{\vec{q}^2} \right\}. \quad (4.9)$$

The above result is known as the ring diagram result<sup>4</sup> - a result which has been obtained by a ring diagram summation. In the case of diagram theory, the factor 1/2 comes from the weight factor for a ring formation and the two terms in the curly brackets represent the ring contributions which start with terms of order  $e'$ . Hence, the last term plays the role of eliminating the first expansion term of the logarithmic function. In our case, it is due to the non-fluctuating term of the Hamiltonian

Note in our result that the free energy is negative. Only when  $k \rightarrow 0$ , the terms in the curly brackets vanish. In this case, the system has the random distribution of Eq. (4.3).

The family of trial weight functions, introduced by Eq. (4.3), may be generalized to

$$g(x; \lambda, \mu) = c e^{-\lambda x^2} x^{2\mu-1}, \quad (4.10)$$

which is characterized by two parameters,  $\lambda$  and  $\mu$ . Following the same prescription, we find

$$F = \frac{1}{2\beta} \sum_{q \neq 0} \left\{ 2 \ln \left[ 1 + \frac{\beta k^2}{2\lambda \vec{q}^2} \right]^\mu - \frac{k^2}{\vec{q}^2} \right\}, \quad (4.11)$$

from which we conclude that unless the condition  $\mu = \lambda$  is satisfied, the free energy will give rise to an infrared divergence. Therefore, for the Gaussian type trial weight functions, the case  $\lambda = \mu = 1/2$  produces the best result.

## 5. CONCLUDING REMARK

We have used a Gaussian trial function as the zeroth approximation. Let us now introduce a small perturbation to this trial function and watch the consequence of it. Let us choose

$$g(x) = \frac{2}{\pi^{1/2}} \frac{e^{-\gamma^2/4}}{1-\text{erf}(\gamma/2)} \exp[-x^2 - \gamma x], \quad (5.1)$$

where  $\gamma$  is a small perturbation parameter, and  $\text{erf}(\gamma/2)$  the error function.

Following the same prescription given in the previous section, the free energy in the next approximation is given by

$$e^{-\beta F} = \sum_{\vec{q} \neq 0} \frac{\exp\left[-\frac{\gamma^2}{4} \left(1 - \frac{1}{1+A}\right) + \frac{\beta \mu(\vec{q})}{2}\right]}{(1+A)^{1/2}} \cdot \frac{1 - \text{erf}[\gamma/2(1+A)^{1/2}]}{1 - \text{erf}(\gamma/2)}, \quad (5.2)$$

where

$$A = k^2/\vec{q}^2. \quad (5.3)$$

For small  $\gamma$ , the error function can be expanded. We find then

$$F = \frac{1}{2\beta} \sum_{\vec{q} \neq 0} \left\{ \ln \left[ 1 + \frac{k^2}{\vec{q}^2} \right] - \frac{k^2}{\vec{q}^2} + h(\gamma, \vec{q}) \right\}, \quad (5.4)$$

where

$$h(\gamma, \vec{q}) = \frac{\gamma}{4} \left(1 - \frac{1}{1+A}\right) \left(1 - \frac{2}{\pi}\right) \left\{ \gamma - \frac{4}{\pi^{1/2}} \frac{\left(1 - \frac{2}{\pi}\right)^{-1}}{1 + (1+A)^{-1/2}} \right\}. \quad (5.5)$$

Note that  $h(\gamma, \vec{q}) < 0$ . The minimum of  $h(\gamma, \vec{q})$  occurs at

$$\gamma = \gamma_0 = \frac{2\pi^{1/2}}{\pi-2} \frac{(1+A)^{1/2}}{1+(1+A)^{1/2}}, \quad (5.6)$$

with the minimum value

$$h(\gamma_0, \vec{q}) = -\frac{A}{\pi-2} [1 + (1+A)^{1/2}]^{-2}. \quad (5.7)$$

Using this minimum value, we find the total perturbation to the free energy, due to the  $\gamma$  term, to be

$$4\pi \int q^2 h(\gamma_0, \vec{q}) d\vec{q} = \frac{4\pi}{\pi-2} \left[ \frac{4}{15} k^3 - \frac{ne^2}{4} \int_0^\infty u(\vec{q}) d\vec{q} \right]. \quad (5.8)$$

The last term makes the integral negative, but has to be set equal to zero because of charge neutrality.

Therefore, the free energy of the system will increase by the first term of Eq. (5.8). It is very interesting to observe that this increase is proportional to  $k^3$  as in the case of the Debye-Hückel free energy.

We have observed essentially the same property with the trial function

$$g(x) = \frac{4\gamma^{1/2} \exp(-1/8\gamma)}{K_{1/4}(1/8\gamma)} \exp(-x^2 - \gamma x^4).$$

Therefore, it seems that the Gaussian trial function was indeed a very good one.

## REFERENCES

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4. See, e.g., Ref.3, p.145.
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