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Inequalities and variational methods in classical statistical mechanics

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Abstract. It is shown that a functional inequality may be used to establish variational principles for partition functions and distribution functions. The inequalities relate distribution functions of higher order to those of lower order. They can be used to suggest approximate integral equations for distribution functions, to test and modify approximate distribution functions, and to establish variational principles on which can be based the systematic computation of distribution functions by variation of parameters.

1. Introduction

It is well known that even for a system consisting of one type of molecule, interacting by means of two-body central forces only, the calculation of distribution functions of value greater than unity is a problem of considerable difficulty. Recently the method of functional Taylor series has afforded some insight into the derivation of two-particle distribution functions (Percus 1962). Nevertheless, it is depressing that even this powerful mathematical tool has provided little more than a systematic derivation of integral equations already known. This paper attempts to widen the spectrum of methods used to attack this problem by establishing variational principles on which the calculation of distribution functions can be based. In § 2 the basic inequality on which the work is based is established. In §§ 3 and 4 it is applied to two systems which differ only by having a different form of interaction potential. The idea is to calculate the properties of one system from those of the other, which are assumed to be known. This is done by establishing inequalities between the properties of the two systems, so that the properties of one system can be used as trial functions in a variational calculation. In § 5 the same basic inequality is used to compare two systems, but we use instead the artifice of distinguishing between the two by introducing into one system a particle at the origin. The relations established in this section are more general, and of the work in this paper may be the most useful in establishing a different approach to the problem of calculating distribution functions.

2. The basic inequality

Consider a variable x which is distributed according to a probability distribution $p(x)$. If, in the usual way, we define

$$\langle x \rangle = \int p(x) x \, dx \tag{1}$$

a function $f(x)$ may be expanded about the value $\langle x \rangle$ by Taylor's theorem:

$$f(x) = f(\langle x \rangle) + (x - \langle x \rangle) f'(\langle x \rangle) + \frac{1}{2!}(x - \langle x \rangle)^2 f''(\xi) \tag{2}$$

where

$$x < \xi < \langle x \rangle .$$

If equation (2) is now averaged with probability distribution $p(x)$, we have

$$\langle f(x) \rangle = f(\langle x \rangle) + \frac{1}{2!} \langle (x - \langle x \rangle)^2 f''(\xi) \rangle . \tag{3}$$

If $f''(\xi)$ is always greater than 0, the last term is always positive. Hence, under these conditions

$$\langle f(x)\rangle \geqslant f(\langle x\rangle). \tag{4}$$

Equation (4) is essentially the variational principle used by Feynman (1955); we shall refer to it as the basic inequality.

3. Inequalities and variational principles for the partition function

The configurational partition function Z of a system of N particles interacting by means of a two-body potential $u(\mathbf{r}_i, \mathbf{r}_j)$ is defined by

$$Z = \int \dots \int d\mathbf{r}_1 \dots d\mathbf{r}_N \exp\left\{-\tfrac{1}{2}\beta \sum_{i,j=1}^{N} u(\mathbf{r}_i, \mathbf{r}_j)\right\}. \tag{5}$$

Now let us consider a second system with interaction potential $u'(\mathbf{r}_i, \mathbf{r}_j)$ and corresponding partition function Z'. We shall consider the primed system as the one whose partition function is known. We may write

$$\frac{Z}{Z'} = \int \dots \int d\mathbf{r}_1 \dots d\mathbf{r}_N (Z')^{-1} \exp\left\{-\tfrac{1}{2}\beta \sum_{i,j=1}^{N} u'(\mathbf{r}_i, \mathbf{r}_j)\right\} \times \left(\exp\left[-\tfrac{1}{2}\beta \sum_{i,j=1}^{N} \{u(\mathbf{r}_i, \mathbf{r}_j) - u'(\mathbf{r}_i, \mathbf{r}_j)\}\right]\right). \tag{6}$$

Defining

$$U = \sum_{i,j=1}^{N} u(\mathbf{r}_i, \mathbf{r}_j) \tag{7a}$$

$$U' = \sum_{i,j=1}^{N} u'(\mathbf{r}_i, \mathbf{r}_j) \tag{7b}$$

$$x = \sum_{i,j=1}^{N} \{u(\mathbf{r}_i, \mathbf{r}_j) - u'(\mathbf{r}_i, \mathbf{r}_j)\} \tag{7c}$$

we may regard $(Z')^{-1} \exp\{-\tfrac{1}{2}\beta U')\}$ as a normalized probability distribution for the variable x, with expectation (we introduce an obvious notation)

$$\langle x\rangle' = (Z')^{-1} \int d\mathbf{r}_1 \dots d\mathbf{r}_N x \exp\{-(\tfrac{1}{2}\beta U')\}. \tag{8}$$

If we put

$$f(x) = \exp\{-(\tfrac{1}{2}\beta x)\} \tag{9}$$

clearly $f''(x) \geqslant 0$. Therefore the basic inequality is valid and

$$\langle f(x)\rangle' \geqslant f\langle x\rangle'. \tag{10}$$

Equation (6), therefore, leads to

$$\frac{Z}{Z'} \geqslant \exp\{-(\tfrac{1}{2}\beta\langle x\rangle')\}. \tag{11}$$

If we put $Z = \exp(-Z') = \exp(-\beta A_0)$, the inequality may be written

$$A_0 \leqslant A_0' + \tfrac{1}{2}\langle x\rangle'. \tag{12}$$

This relation may be used as the basis of a variational principle for computing the partition function. The properties of the primed system—for example the interparticle potential—can be expressed in terms of arbitrary parameters which can be varied until the right-hand side of equation (12) reaches a minimum value.

4. Inequalities and variational principles for the distribution functions

We define the generic probability distributions by

$$n_S(\mathbf{r}_1 \ldots \mathbf{r}_S) = \frac{N! \int d\mathbf{r}_{S+1} \ldots d\mathbf{r}_N \exp\{-(\beta U)\}}{(N-S)! \int d\mathbf{r}_1 \ldots d\mathbf{r}_N \exp\{-(\beta U)\}}. \tag{13}$$

The function

$$\exp\{-(\tfrac{1}{2}\beta U')\}\left[\int \ldots \int d\mathbf{r}_{S+1} \ldots d\mathbf{r}_N \exp\{-(\tfrac{1}{2}\beta U')\}\right]^{-1}$$

may be regarded as a normalized distribution function for the variables $\mathbf{r}_{S+1} \ldots \mathbf{r}_N$. Using an obvious notation, equation (10) can be extended to

$$\langle f(x) \rangle_S' \geqslant f(\langle x \rangle_S'). \tag{14}$$

Defining $n_S'(\mathbf{r}_1 \ldots \mathbf{r}_S)$ to be the distribution corresponding to potential $u'(\mathbf{r}_i, \mathbf{r}_j)$ we have, from (12),

$$\frac{n_S(\mathbf{r}_1 \ldots \mathbf{r}_S)}{n_S'(\mathbf{r}_1 \ldots \mathbf{r}_S)} = \frac{Z'}{Z} \int \ldots \int d\mathbf{r}_{S+1} \ldots d\mathbf{r}_N \exp(-\tfrac{1}{2}\beta) \frac{\exp\{-(\frac{1}{2}\beta U')\}}{\int d\mathbf{r}_{S+1} \ldots d\mathbf{r}_N \exp\{-(\frac{1}{2}\beta U')\}}. \tag{15}$$

Application of inequality (14) gives

$$\ln \left\{\frac{n_S(\mathbf{r}_1 \ldots \mathbf{r}_S)}{n_S'(\mathbf{r}_1 \ldots \mathbf{r}_S)}\right\} \frac{Z}{Z'} \geqslant -\tfrac{1}{2}\beta \langle x \rangle_S'. \tag{16}$$

In terms of variables $n_S(\mathbf{r}_1 \ldots \mathbf{r}_S) = \exp\{-\beta A_S(\mathbf{r}_1 \ldots \mathbf{r}_S)\}$. This may be written conveniently as

$$A_S \leqslant A_S' + A_0' - A + \tfrac{1}{2}\langle x \rangle_S'. \tag{17}$$

The relation (17) may be used as the basis of a variational principle for the determination of the distribution functions n_S. The variation of the functions is subject to the equations of constraint imposed by the normalization conditions on the distribution functions.

5. Variational principles and integral equations

We now consider essentially the same equations as before, but with different meanings for the primed and unprimed systems. We take the primed system as homogeneous, consisting of N particles. The unprimed system is formed by adding to the primed system a single particle at the origin. The same device is used in the functional expansion method (Percus 1962). In this case

$$\sum_{i,j=1}^{N} \{u(\mathbf{r}_i, \mathbf{r}_j) - u'(\mathbf{r}_i, \mathbf{r}_j)\} = \sum_{i=1}^{N} u(\mathbf{r}_0, \mathbf{r}_i). \tag{18}$$

Therefore

$$\left\langle \sum_{i=1}^{N} u(\mathbf{r}_0, \mathbf{r}_i) \right\rangle' = \int d\mathbf{r}_1 n_1'(\mathbf{r}_1) u(\mathbf{r}_0, \mathbf{r}_1).$$

Hence the analogue of equation (12) is

$$A_0 < A_0' + \int d\mathbf{r}_1 n_1'(\mathbf{r}_1) u(\mathbf{r}_0, \mathbf{r}_1). \tag{19}$$

This equation does not seem very useful as the second term will diverge for many practical potentials. The right-hand side of (16), on the other hand, is replaced by

$$-\beta \left\{\sum_{i=1}^{S} u(\mathbf{r}_0, \mathbf{r}_i) + \frac{1}{n_S'(\mathbf{r}_1 \ldots \mathbf{r}_N)} \int d\mathbf{r}_{S+1} u(\mathbf{r}_0, \mathbf{r}_{S+1}) n_{S+1}'(\mathbf{r}_1 \ldots \mathbf{r}_{S+1})\right\}.$$

From the definitions (13) the addition of a particle at the origin changes $n_S'(\mathbf{r}_1 \dots \mathbf{r}_S)$ to $n_{S+1}'(r_0 \dots r_S)/n_0'(r_0)$. Hence the inequality (16) becomes

$$\ln\left\{\frac{n_{S+1}'(\mathbf{r}_0 \dots \mathbf{r}_S)}{n_S'(\mathbf{r}_1 \dots \mathbf{r}_S)n_0'(\mathbf{r}_0)}\frac{Z}{Z'}\right\} \geqslant -\beta\left\{\sum_{i=1}^{S} u(\mathbf{r}_0, \mathbf{r}_i) + \frac{1}{n_S'(\mathbf{r}_1 \dots \mathbf{r}_S)}\int d\mathbf{r}_{S+1}u(\mathbf{r}_0, \mathbf{r}_{S+1})n_{S+1}'(\mathbf{r}_1 \dots \mathbf{r}_{S+1})\right\} \tag{20}$$

or

$$A_{S+1}'(\mathbf{r}_0 \dots \mathbf{r}_S) < A_S'(\mathbf{r}_1 \dots \mathbf{r}_S) + A_0' - A_0 + A_1 + \beta\left\{\sum_{i=1}^{S} u(\mathbf{r}_0, \mathbf{r}_i) + \frac{1}{n_S(\mathbf{r}_1 \dots \mathbf{r}_S)}\int d\mathbf{r}_{S+1}u(\mathbf{r}_0, \mathbf{r}_{S+1})n_{S+1}'(\mathbf{r}_1 \dots \mathbf{r}_{S+1})\right\}. \tag{21}$$

The relation (21) is a general inequality which must be satisfied by any distribution functions. If the distribution function of lower order is known, a trial function $A_{S+1}''(\mathbf{r}_0 \dots \mathbf{r}_S)$, which corresponds to a trial number distribution $n_{S+1}''(\mathbf{r}_0 \dots \mathbf{r}_S)$, may be defined by

$$A_{S+1}''(\mathbf{r}_0 \dots \mathbf{r}_S) = A_S'(\mathbf{r}_1 \dots \mathbf{r}_S) + A_0' - A_0 + A_1' + \beta\left\{\sum_{i=1}^{S} u(\mathbf{r}_0, \mathbf{r}_i) + \frac{1}{\bar{n}_S'(\mathbf{r}_1 \dots \mathbf{r}_S)}\int d\mathbf{r}_{S+1}u(\mathbf{r}_0, \mathbf{r}_{S+1})n_{S+1}''(\mathbf{r}_1 \dots \mathbf{r}_{S+1})\right\}. \tag{22}$$

The relation (21) then assures us that $A_{S+1}'' > A_{S+1}'$, so that (21) is the basis of a variational principle for determination of distribution functions in terms of those of order one lower.

The relation (20) is of particular interest for $S = 1$. In this case we obtain, putting

$$g'(\mathbf{r}_1, \mathbf{r}_2) = \frac{n_2'(\mathbf{r}_1, \mathbf{r}_2)}{n_1'(\mathbf{r}_1)n_2'(\mathbf{r}_2)}$$

$$\ln\left\{g'(\mathbf{r}_0, \mathbf{r}_1)\frac{Z}{Z'}\right\} \geqslant -\beta\left\{u(\mathbf{r}_0, \mathbf{r}_1) + n_0'(\mathbf{r}_0)\int d\mathbf{r}_2 u(\mathbf{r}_0, \mathbf{r}_2)g'(\mathbf{r}_2, \mathbf{r}_1)\right\}. \tag{23}$$

Written in the form

$$g'(\mathbf{r}_0, \mathbf{r}_1) \geqslant \frac{Z'}{Z}\exp\left[-\beta\left\{u(\mathbf{r}_0, \mathbf{r}_1) + n'(\mathbf{r}_0)\int d\mathbf{r}_2 u(\mathbf{r}_0, \mathbf{r}_2)g'(\mathbf{r}_2, \mathbf{r}_1)\right\}\right] \tag{24}$$

the relation (24) forms the basis of a variational principle for the determination of the pair correlation functions $g(\mathbf{r}_0, \mathbf{r}_1)$.

If the second term of equation (3) is sufficiently small, the inequality (24) might well be replaced by the equality

$$g'(\mathbf{r}_0, \mathbf{r}_1) = \frac{Z'}{Z}\exp\left[\beta\left\{u(\mathbf{r}_0, \mathbf{r}_1) + n'(\mathbf{r}_0)\int d\mathbf{r}_2\, u(\mathbf{r}_0, \mathbf{r}_2)g'(\mathbf{r}_2, \mathbf{r}_1)\right\}\right] \tag{25}$$

and gives an integral equation for the pair correlation function; the approximation $Z = Z'$ would be an obvious one here. In equation (25), $n'(r_0)$ is, of course, just the number density. More generally, (24) forms the basis of a variational principle for the determination of the pair correlation function by means of a trial function which satisfies equation (25).

6. Conclusion

We have shown in §§ 3 and 4 that the basic inequality established in § 1 may be used to compute, by variational methods, the distribution functions of one system provided that those of a related system, of differing pair potential, are known. One might, for example, attempt to see the modification which would be produced in a hard-sphere model by adding an attractive tail. In § 4 general inequalities which connect a distribution function to one of neighbouring order by means of the pair potential are established. Such inequalities may be used immediately as criteria for the validity of any approximation for the distribution functions. If the inequalities are not satisfied, an immediate improvement can be made to the approximations by the addition of suitable factors (functions of density and temperature) to the distribution functions which ensure that the inequalities are satisfied. More generally, the inequalities lead to a systematic approach to the computation of distribution functions by a variational procedure. A simple form of this replaces the inequalities by equalities; this procedure leads to integral equations for the distribution functions and, as an example, the integral equation for the pair correlation function is obtained.

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References

Feynman, R. P., 1955, *Phys. Rev.*, **97**, 660.
Percus, J. A., 1962, *Phys. Rev. Lett.*, **8**, 462.