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An extension of Gibbs variational principle for canonical partition function

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Abstract

A variational principle is derived based upon the canonical partition functions. This variational principle is obtained using the Gibbs variational principle. Firstly, the Gibbs variational principle is highlighted for the canonical ensemble. Then, the Gibbs variational principle is modified such that a variational principle concerning the partition function is obtained. The latter variational principle is useful as the canonical partition function is an important quantity in deriving many thermodynamic quantities of a physical system based upon the distribution of the constituents that makes up the system.

Key words: variational principle, Gibbs variational principle, partition function

Introduction

Science and technology nowadays are rapidly evolving, including in the field of statistical physics. These developments are observed from the occurrence of many industrial products, which uses statistical physics, such as printer ink, detergent soap, paint, and oil. Because of its importance, both as pure or applied science, fundamental research concerning the statistical physics must be continued.

Statistical mechanics is the application of probability theory dealing with the dynamics of many-particle systems under certain (external) potential. Statistical mechanics specifically provides a framework that bridge between microscopic properties of a system with its macroscopic or thermodynamic properties [1]. In statistical mechanics, one starts from the microscopic description of a system, i.e. the microstates. Then depending on the information wanted, the macro states are constructed from the microstates. Once the energy distribution is obtained, the partition function may be gained. Much suitable thermodynamic information can then be derived as derivatives of the partition function. Hence, the partition function holds a pivotal role in statistical physics. It is through the partition function that the macroscopic information is attained.

A powerful method in order to study physical properties of a system is using the variational principle. In this method, a functional is optimized (may be maximized or minimized). Thus, the quantity which is optimized may be predicted. It is relatively a simple method, but has powerful prediction ability. In this article, the Gibbs variational principle is discussed and extended.

The Gibbs variational principle is formulated by J. Willard Gibbs (1839–1903). Gibbs variational principle is used to determine the energy functional concerning with chemical reaction that may do work. The aforementioned energy is the free energy of a system, i.e. the Helmholtz free energy (F)[2]. The Gibbs variational principle has been used in many articles and researches. The variational principle is used in minimizing the energy and entropy functional, which depend upon the physical quantities of particles in one dimension [3]. Steam engines are also being discussed using the Gibbs variational principle [4].

In this article, the Gibbs variational principle is extended to obtain a partition function variational principle of a physical system. Hence the quantity which is optimized (in this case, maximized) is the partition function, not the Helmholtz free energy. This is certainly interesting in the statistical mechanics point of view, as one do not have to construct the free energy of the system, but just the partition function from the system. Here, we focus on the canonical ensemble where the system may exchange heat, but not particles [1].

Methodology

This article is mainly a theoretical study. Firstly, the Gibbs variational principle is described for canonical ensemble. Then, the extension of the Gibbs variational principle to the canonical partition function is given.

Results and Discussion

We use a variable *f* in the discussion of Gibbs variational principle of the canonical distribution function. The variable f is a normalized distribution function in the quantum system or in the classical system. In the quantum system, it is a Hamiltonian function. In the classical system the function of f has a real and postive value. The normalization of the distribution function can be stated as.

$$\mathrm{Tr}\, f = 1, \qquad (1)$$

where, the trace (Tr) operator is a finite integral over all degrees of freedoms, $\int_0^\infty dpdr$. The elements of dp and dr is the differential element of momentum and position in the phase space.

Next, we define a functional,

$$F(f) \equiv \mathrm{Tr}(Hf) + \mathrm{Tr}\beta^{-1}(f \ln f)$$
$$= \mathrm{Tr}\,(Hf + \beta^{-1} f \ln f), \qquad (2)$$

where H is the hamiltonian and β is equal to kT, k is the Boltzmann's constant, and T is the absolute temperature. This functional is called the Gibbs free energy functional, since, to our knowledge, where originally constructed by Gibbs [1,5].

The first term of the functional (2) is the expectation value of energy. The second term is called Shannon entropy. The Shannon entropy can be written as [6]:

$$S[f] = \left(\frac{\partial F}{\partial T}\right)_V = k\mathrm{Tr} f \ln f. \qquad (3)$$

The Gibbs variational has two principles as stated below.

1. Make $F[f]$ to be a minimum by varying f which satisfy the normatization condition. The function f_0, which has made the

functional $F[f]$ to be a minimum is called the equilibrium distribution function.

2. The Helmholtz free energy is given by $F_0 = F[f_0]$.

A key point to the first principle is to find the first functional derivative of F by f. Thus,

$$\frac{\delta F[f]}{\delta f} = \frac{\delta}{\delta f}\{Tr\,(Hf) + Tr\,\beta^{-1}(f\ln f)\}$$

$$= Tr\,H\,\frac{\delta f(\boldsymbol{r},\boldsymbol{p})}{\delta f(\boldsymbol{r}',\boldsymbol{p}')} + \beta^{-1}Tr\,\frac{\delta f(\boldsymbol{r},\boldsymbol{p})}{\delta f(\boldsymbol{r}',\boldsymbol{p}')}\ln f + \beta^{-1}Tr\,f\,\frac{\delta \ln f}{\delta f}$$

$$= Tr\,H\,\frac{\delta f(\boldsymbol{r},\boldsymbol{p})}{\delta f(\boldsymbol{r}',\boldsymbol{p}')} + \beta^{-1}Tr\,\frac{\delta f(\boldsymbol{r},\boldsymbol{p})}{\delta f(\boldsymbol{r}',\boldsymbol{p}')}\ln f + \beta^{-1}Tr\frac{1}{f}\,f\,\frac{\delta f(\boldsymbol{r},\boldsymbol{p})}{\delta f(\boldsymbol{r}',\boldsymbol{p}')}$$

$$= Tr\,H\delta(\boldsymbol{r}-\boldsymbol{r}',\boldsymbol{p}-\boldsymbol{p}') + \beta^{-1}\,Tr\ln f\;\delta(\boldsymbol{r}-\boldsymbol{r}',\boldsymbol{p}-\boldsymbol{p}') + \beta^{-1}\,Tr\,\delta(\boldsymbol{r}-\boldsymbol{r}',\boldsymbol{p}-\boldsymbol{p}')$$

$$= H(\boldsymbol{r}',\boldsymbol{p}') + \beta^{-1}\ln f(\boldsymbol{r}',\boldsymbol{p}') + \beta^{-1}.1$$

$$= H(\boldsymbol{r}',\boldsymbol{p}') + \beta^{-1}(\ln f(\boldsymbol{r}',\boldsymbol{p}') + 1)$$

$$= H + \beta^{-1}(\ln f + 1). \qquad (4)$$

Hence, the first functional derivative of *F* yields the Hamiltonian and the entropy, respectively, in the first and second term. Then, we would like to inspect the extreme value of the functional. The type of extreme value (maximum, minimum, or inflection) can be found by finding the second derivative of the functional, i.e.

$$\frac{\partial}{\partial f}\left[\frac{\delta F[f]}{\delta f}\right] = \frac{\partial}{\partial f}H + \beta^{-1}\frac{\partial}{\partial f}\ln f + \beta^{-1}\frac{\partial}{\partial f}1$$

$$= 0 + \frac{1}{f}\beta^{-1} + 0$$

$$= (\beta f)^{-1}. \qquad (5)$$

The value of β as well as f is positive. Thus, the result of equation (5) satisfies,

$$(\beta f)^{-1} > 0. \qquad (6)$$

The second derivative of the functional $F[f]$ is positive, so the functional has a minimum value. To find the minimum value of functional (2), we define a Lagrange multiplier λ. Thus,

$$\left[\frac{\delta}{\delta f}(F + \lambda\,Trf)\right]_{f=f_0} = 0.$$

Considering again the result of the first functional derivative in (4), we obtain,

$$H + \beta^{-1}(\ln f_0 + 1) + \lambda = 0,$$

or

$$f_0 = e^{-\beta H} e^{-(\beta\lambda+1)}. \quad (7)$$

f_0 which is given in equation (7) is the equilibrium canonical distribution function that minimizes F. Function f_0 still contains Lagrange multiplier λ. We should eliminate λ by operating trace on the both side of equation (7) and then using the normalization equation (1), we get,

$$Trf_0 = Tr\left(e^{-\beta H} e^{-(\beta\lambda+1)}\right).$$

Because β and λ are constants (do not depend on the degrees of freedoms), they may be taken out of trace, yielding,

$$1 = \frac{Tre^{-\beta H}}{e^{(\beta\lambda+1)}},$$

or

$$e^{-(\beta\lambda+1)} = Tre^{-\beta H}. \quad (8)$$

Substituting equation (8) to the equation (7), gives:

$$f_0 = \frac{e^{-\beta H}}{Tr\, e^{-\beta H}}. \quad (9)$$

Again, equation (9) is the equilibrium canonical distribution function, but now without the Lagrange multiplier λ, this proves the first Gibbs variational principle. To prove the second Gibbs variational principle, we substitute equation (9) to the functional (2), thus:

$$F[f_0] = Tr(Hf_0) + Tr\beta^{-1} f_0 \ln f_0$$

$$= Tr\left(\frac{He^{-\beta H}}{Tre^{-\beta H}}\right) + Tr\beta^{-1}\frac{e^{-\beta H}}{Tre^{-\beta H}} \ln \frac{e^{-\beta H}}{Tre^{-\beta H}}$$

$$F[f_0] = -\beta^{-1} \ln Tre^{-\beta H}. \quad (10)$$

$F[f_0]$ is the Helmholtz free energy as stated in the second Gibbs variational principle.

We can determine the Lagrange multiplier by putting a logarithmic function in both sides of the equation (8), giving:

$$-\beta^{-1} \ln e^{(\beta\lambda+1)} = -\beta^{-1} \ln Tre^{-\beta H}$$
$$-\beta^{-1}(\beta\lambda + 1) = F_0,$$

or

$$\lambda = -\beta^{-1} - F_0. \quad (11)$$

Due to the first Gibbs variational principle, f_0 is a function that makes the functional F to be a minimum. Thus, the following inequality holds,

$$F[f] > F[f_0], \qquad f \neq f_0. \quad (12)$$

So,

$$F[f_0] \leq F[f]$$

$$-\beta^{-1} \ln Tre^{-\beta H} \leq Tr(Hf) + Tr\beta^{-1}(f \ln f)$$

$$Tre^{-\beta H} \geq e^{-\beta\{Tr(Hf) + Tr\beta^{-1}(f \ln f)\}}. \quad (13)$$

It can be observed that the left hand side of the inequality (13) is just the partition function Q_0. Hence, the inequality becomes:

$$Q_0 \geq e^{-\beta\{Tr(Hf) + Tr\beta^{-1}(f \ln f)\}}. \quad (14)$$

The right hand side of inequality (14) is a functional of *f*. It is the partition functional or

$$Q_0 \geq Q[f], \quad (15)$$

where

$$Q[f] = e^{-\beta\{Tr(Hf) + Tr\beta^{-1}(f \ln f)\}}. \quad (16)$$

The equality is obtained if $f = f_0$, such that $Q_0 = Q[f_0]$. This is the extension of Gibbs variational principle for canonical partition function. Here instead of the Helmholtz free energy we have the canonical partition functional. Furthermore, we can expand the exponential terms of equation (16) in a series, that is,

$$e^{-\beta\{Tr(Hf)+Tr\beta^{-1}(f\ln f)\}} = 1 - \beta\{Tr(Hf) + Tr\beta^{-1}(f\ln f)\} + \frac{\beta^2\{Tr(Hf) + Tr\beta^{-1}(f\ln f)\}^2}{2!} + \cdots$$

If we then use only the first and second terms of the above equation, we get:

$$Q[f] = 1 - \beta Tr(Hf + \beta^{-1}f\ln f)$$
$$= 1 - \beta Tr(Hf) - Tr(f\ln f). \quad (18)$$

Thus, we obtain the canonical partition functional. This quantity can be used to determine many thermodynamic quantities.

Conclusion

The partition functional for the canonical ensemble can be obtained through Gibbs variational principle. The partition function satisfies the inequality (14).

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