

Molecular Modeling and Simulation  
Applications and Perspectives

Jianzhong Wu *Editor*

# Variational Methods in Molecular Modeling

 Springer

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Applications and Perspectives

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Jianzhong Wu  
Editor

# Variational Methods in Molecular Modeling

 Springer

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## Series Editor's Preface

The series *Molecular Modeling and Simulation—Application and Perspectives* seeks to publish a comprehensive collection of volumes highlighting the most important and groundbreaking developments in molecular modeling and simulation. The goal is to publish volumes where leading researchers can describe the latest advances in their field in a comprehensive and nuanced manner that makes the material both accessible to those outside the field while at the same time being useful to other experts. The series encourages authors to expand their treatment of their topic in ways that are impossible to achieve in normal journal articles. With this second volume in the series “Variational Methods in Molecular Modeling,” Editor Jianzhong Wu has assembled an outstanding collection of contributions from the top people in the field of variational methods. The volume starts with a pedagogical introduction to the topic that should be of great interest to students desiring to learn about these methods. In the subsequent nine chapters, the authors provide an overview of variational methods for the particular topic of their chapter and follow this with examples that illustrate the application of these methods. The volume closes with an appendix treating the calculus of variations.

I am deeply grateful to Prof. Jianzhong Wu of the University of California, Riverside, for his willingness to take on this project and for his wisdom and effort in putting together such an outstanding volume. I am confident this volume will play an important role in the future application of these methods to the field of molecular modeling.

Edward Maginn  
University of Notre Dame

# Preface

Calculus of variations is a branch of mathematical analysis that deals with functionals, i.e., algebraic relations mapping functions into real numbers. The original ideas were established by Leonhard Euler in 1733, and since then, variational methods have found widespread applications in science and engineering. A key objective in the calculus of variations is to identify a specific function that minimizes (or maximizes) a given functional. The mathematical procedure is naturally applicable to statistical thermodynamics as demonstrated in the groundbreaking works of J. Willard Gibbs. Today, the maximum entropy principle (MaxEnt), a cornerstone of the so-called Bayesian statistics, is broadly used not only in equilibrium as well as non-equilibrium statistical mechanics but also in pattern recognition and image processing, risk analysis, urban and regional planning, and business financing, just to name a few from a large class of probabilistic problems. Calculus of variations is also useful in both classical and quantum mechanics as shown in the pioneering works of Joseph-Louis Lagrange and in the variational principle for determining the ground states of quantum systems.

This monograph is an exposition of recent applications of variational methods in molecular modeling for thermodynamic systems. While variational principles have been routinely used in both Lagrangian mechanics and the Kohn–Sham density functional theory, their applications to complex molecular systems are rarely discussed in the conventional texts of molecular modeling and statistical mechanics. Instead of describing molecular motions and electronic structures, this book is mostly concerned with the formulation and application of free-energy functionals that connect thermodynamic variables with potential fields or the ensemble averaged atomic, molecular, or particle distributions. Prime examples include classical density functional theory for simple as well as complex fluids, self-consistent-field theories for ionic mixtures and polymer blends, phase-field methods for phase separations and interfacial phenomena, and the Ginzburg-Landau-type theories for molecular self-assembly and order-disorder transitions. In addition, this book covers the applications of variational methods to describing time-dependent phenomena and to solving quantum many-body problems.

To introduce these fascinating topics to a broad audience, each chapter in this book provides a pedagogical overview of variational methods for specific subjects, with the key theoretical results illustrated with tutorial examples. With emphasis placed on physical understanding rather than on rigorous mathematical derivations, this monograph should be accessible to graduate students and researchers in the broad areas of applied mathematics, condensed matter physics, materials science and engineering, chemistry, and chemical and biomolecular engineering without specific training in the calculus of variations.

I am tremendously grateful to all contributors of this monograph for their dedicated work and cooperation in finishing their writings in a timely manner. Preparation of pedagogical materials is not most rewarding in today's academic environment, yet it is very time-consuming to summarize the previous research in particular publications from others. Therefore, I feel especially lucky to have contributions to this book from a cohort of very distinguished authors. I also want to thank all reviewers of this monograph for their careful examination of individual chapters and professional services: Jaydeep P. Bardhan, Northeastern University; Daniel Borgis, École Normale Supérieure; Joachim Dzubiella, Humboldt University; Jian Jiang, California Institute of Technology; Isamu Kusaka, Ohio State University; Yu Liu, East China University of Science and Technology; Umberto M.B. Marconi, University of Camerino; Friederike Schmid, University of Mainz; Cyrus Umrigar, Cornell University; Qiang (David) Wang, Colorado State University; Rik Wensink, University of Paris-Sud XI; Zhenli Xu, Shanghai Jiao Tong University; and Pingwen Zhang, Peking University. Last, but not least, I would like to thank Prof. Edward Maginn, the Chief Editor of this book series, for inviting me to prepare this monograph and Mr. Praveen Kumar, the Springer Project Coordinator, for his considerable help and patience to put things together.

Riverside, CA, USA

Jianzhong Wu



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# Variational Methods in Statistical Thermodynamics—A Pedagogical Introduction

Zhen-Gang Wang

## 1 Introduction

In this chapter, we provide a pedagogical introduction to variational methods in statistical thermodynamics. This chapter is written primarily for graduate students who have had a first course in statistical mechanics. It is hoped that this chapter provides a useful and insightful introduction to both the conceptual and practical aspects of the variational methods that can be helpful in their research in statistical mechanics.

Variational principle is at the very heart of thermodynamics. Its root is the second law, usually stated in terms of the entropy, which is an inequality—the only fundamental physical law that takes the form of an inequality rather than equality [1]. The statistical mechanical correspondence of the variational method is the maximum-term method in the evaluation of the partition function, which forms the basis for minimization of the free energy. We thus start with a brief review of the variational nature of thermodynamics and its corresponding statistical mechanical origin.

Except for a limited number of special cases, the partition function cannot be evaluated exactly. Thus in constructing the free energy of a system of interest, we usually have to make approximations. One of the simplest and most useful approximations is the mean-field approximation, which in essence reduces an intractable many-body problem to a single-body problem in an effective external field, which is then determined self-consistently. While for simple systems, the mean-field approximation can often be constructed intuitively, more systematic derivations are based on variational methods. We present two common variational methods for approximating the partition function (or equivalently the free energy)—the Gibbs-Bogoliubov-Feynman (GBF) variational bound, and the steepest-descent method. By way of a toy example in the evaluation of an integral, we illustrate the use of these two methods. We then

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use the variational methods to derive the mean-field solution for the Ising model and the Poisson-Boltzmann theory for electrolyte solutions. Finally, we show that the GBF method provides a natural way to include fluctuation effects in weakly correlated systems.

## 2 The Variational Nature of Thermodynamics

The second law of thermodynamics is commonly expressed by the Clausius inequality:

$$dS \geq \frac{\delta Q}{T} \quad (2.1)$$

where  $S$  is the entropy of the system,  $Q$  the heat into the system and  $T$  the absolute temperature. In the most general case the temperature refers to that of the heat bath. For an adiabatic process, the right hand side of the expression is zero, and Eq. 2.1 reduces to the well-known expression

$$dS \geq 0 \quad (2.2)$$

This is often termed the principle of increasing entropy. If we consider the system and surrounding as a closed, isolated system, then this principle states that the entropy cannot decrease—it increases for an irreversible (nonequilibrium) process and reaches a maximum at equilibrium.

The principle of increasing entropy implies a variational principle. Imagine we start an isolated system in some nonequilibrium state, then the second law tells us that the state of the system will evolve in such a way as to increase its entropy. However, if the system is to finally attain a well defined final equilibrium, as postulated in thermodynamics, then the entropy will asymptotically reach a final value—the maximum value—and cease to increase. Since the entropy is at its maximum in this final state, its first differential with respect to any real or virtual change in the macro states of the system (for example, the density distribution in a gas in the absence of external fields) must vanish, while its second differential will be negative. Thus mathematically, the condition of equilibrium for an isolated system is expressed as:

$$\frac{\delta S}{\delta X} = 0 \quad (2.3)$$

and

$$\frac{\delta^2 S}{\delta X^2} < 0 \quad (2.4)$$

where we use the generic notation  $X$  to denote some unconstrained macrostate variable [2]. The second derivative is usually unnecessary (it rarely is explicitly evaluated), as the problem statement usually makes it obvious whether the extreme is a

maximum or minimum. Henceforth we will focus on the first derivative. For simplicity, we consider here only one variable, but generalization to multivariables is straightforward.

Isolated systems are not the most convenient systems to work with. In most cases, the system of interest is in thermal contact with a heat bath. Heat bath or reservoir is an idealized conceptual construct in thermodynamics. Its size is considered sufficiently large (in fact infinite) and is always in its own internal equilibrium. These two attributes imply that any finite change in its extensive variables, such as energy, volume, particle number, are infinitesimal processes for the bath, so that it is always maintained at internal equilibrium and its intensive properties, such as temperature, pressure, or chemical potential, remain unchanged.

For an isothermal process where the system is kept in thermal equilibrium with a thermal bath (thus having the same temperature as the thermal bath), making use of the first law  $dE = \delta Q + \delta W$ , the Clausius inequality becomes

$$d(TS) \geq dE - \delta W \quad (2.5)$$

or

$$d(E - TS) \leq \delta W \quad (2.6)$$

(We use  $E$  rather than  $U$  as the notation for the energy of the system because  $E$  is the more common notation in statistical mechanics.) Equation 2.6 naturally leads to the definition of the Helmholtz free energy:

$$F = E - TS \quad (2.7)$$

In terms of the Helmholtz free energy, the second law now becomes

$$dF \leq \delta W \quad (2.8)$$

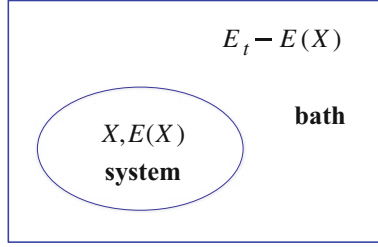
In the special case of no work, we thus have

$$dF \leq 0 \quad (2.9)$$

Therefore, for an isothermal system, the Helmholtz free energy will decrease for a spontaneous process and will reach a minimum at equilibrium. Following similar arguments as for entropy, the equilibrium condition in terms of the Helmholtz free energy is

$$\frac{\delta F}{\delta X} = 0 \quad (2.10)$$

We can obtain Eq. 2.10 using an alternative approach, which serves to illustrate the use of the variational condition on the entropy, Eq. 2.3. Recall that the maximum entropy condition is for an isolated system. Therefore, to make use of Eq. 2.3, we



**Fig. 1** Isothermal system (enclosed within the *oval*) in contact with the thermal bath. The system and the bath can be considered an isolated “super” system whose boundary is indicated by the *rectangle*. The bath is assumed to be much larger in extent and so  $E_t \gg E(X)$

consider a “super system” consisting of the system of interest and the bath; see Fig. 1 for illustration. Let the total energy of the super system be  $E_t$ , the energy of the system of interest be  $E$ . We use  $X$  to denote the unconstrained internal macrostate variable for the system. In general, the system energy depends on  $X$ , and we write  $E(X)$  to account for this dependence. The total entropy of the super system is then

$$S_t [E(X), X; E_t] = S [E(X), X] + S_b [E_t - E(X)] \quad (2.11)$$

Because the bath is much larger than the system, we may Taylor expand the last term around  $E_t$ . Doing so yields,

$$S_t [E(X), X; E_t] = S [E(X), X] + S_b (E_t) - \left( \frac{\partial S_b}{\partial E_b} \right)_{E_b=E_t} E(X) \quad (2.12)$$

We recognize that the derivative  $(\partial S_b / \partial E_b)$  is nothing but the inverse of the temperature of the bath, so

$$S_t [E(X), X; E_t] = S [E(X), X] - \frac{E(X)}{T_b} + S_b (E_t) = -\frac{F(X)}{T_b} + S_b (E_t) \quad (2.13)$$

where  $F(X) = E(X) - T_b S [E(X), X]$  is just the Helmholtz free energy of the system at the isothermal condition when the system temperature is kept at the bath temperature. Since the last term is an immaterial constant independent of the system variables, the condition of maximum in  $S_t$  for the super system is equivalent to the condition of minimum in  $F$  for the system.

Variational conditions using other thermodynamic potentials can be derived following similar arguments. Of particular interest is the variational condition using the grand potential, which for a single-component system, is defined as

$$W [N(X), X] = F [N(X), X] - \mu_b N(X) \quad (2.14)$$

where  $\mu_b$  is the chemical potential of the particle reservoir (bath).  $X$ , for example, can be the density distribution of the particles. The grand potential is convenient for treating systems with spatial inhomogeneity as well as for describing phase transitions, because the temperature and chemical potential of the system are set by the reservoir (i.e., do not need to be solved for), so equality of chemical potential is automatically satisfied.

### 3 The Variational Origin of Statistical Thermodynamics

The central task of statistical thermodynamics is the computation of the partition function in a given ensemble, from which we obtain the appropriate thermodynamic potential (free energy) and all other equilibrium thermodynamic properties. The most common ensemble is the canonical ensemble at fixed volume, particle number and temperature (set by the thermal bath). Symbolically, we write the canonical partition function as:

$$Q = \int d\Gamma \exp[-\beta H(\Gamma)] \quad (3.1)$$

where  $\Gamma$  is a collective symbol to denote the microstates of the system,  $H$  is the Hamiltonian, and  $\beta = (kT)^{-1}$  with  $T$  being the temperature of the bath.  $\int d\Gamma$  is a short-hand notation for summing over the microstates. For example, in the case of classical fluids, it denotes summing over all the particle momenta and positions. For the Ising model, it corresponds to summing over all spin states.

From the partition function, we obtain the free energy as

$$F = -kT \ln Q = -kT \ln \left\{ \int d\Gamma \exp[-\beta H(\Gamma)] \right\} \quad (3.2)$$

To see the connection to variational principle, we perform the summation over the microstates in two steps. First, we group all the microstates that correspond to a particular value of the macrostate  $X$ , and then we sum over the value of the macrostate  $X$ . Mathematically, this is accomplished by inserting the following identity  $\int dX \delta[X - \hat{X}(\Gamma)] = 1$  into the partition function

$$Q = \int d\Gamma \int dX \delta[X - \hat{X}(\Gamma)] \exp[-\beta H(\Gamma)] = \int dX \int d\Gamma \delta[X - \hat{X}(\Gamma)] \exp[-\beta H(\Gamma)] \quad (3.3)$$

Where  $\hat{X}(\Gamma)$  is the microscopic definition of  $X$  in terms of the microstate  $\Gamma$ . The inner integral over  $\Gamma$  yields a constrained partition function

$$Q(X) = \int d\Gamma \delta[X - \hat{X}(\Gamma)] \exp[-\beta H(\Gamma)] \quad (3.4)$$



from which we can define a constrained free energy

$$F(X) = -kT \ln Q(X) \quad (3.5)$$

Thus, the partition function now becomes

$$Q = \int dX \exp [-\beta F(X)] \quad (3.6)$$

$F(X)$  defines a free energy surface in the macrostate variable  $X$ ; it is a constrained free energy for a fixed value of the internal variable  $X$ . In general  $F(X)$  is some highly nonlinear function of  $X$  and as such the integral cannot be evaluated exactly. Here we use Laplace's method [3], by noting that the integral will be dominated by values of  $X$  around the maximum of the integrand, or the minimum of the free energy  $F(X)$ . Denoting by  $X^*$  the value of  $X$  at the minimum, it is obtained from

$$\frac{\partial F(X)}{\partial X} = 0 \quad (3.7)$$

Expanding  $F(X)$  around  $F(X^*)$  to quadratic order, we get

$$F(X) = F(X^*) + \frac{1}{2} F^{(2)}(X - X^*)^2 \quad (3.8)$$

where  $F^{(2)}$  is the second derivative evaluated at  $X = X^*$ . Performing the straightforward Gaussian integral, we obtain

$$Q = \sqrt{\frac{2\pi}{F^{(2)}}} \exp [-\beta F(X^*)] \quad (3.9)$$

The equilibrium free energy is then

$$F = -kT \ln Q = F(X^*) + \frac{1}{2} kT \ln \frac{F^{(2)}}{2\pi} \quad (3.10)$$

Because the free energy is extensive, i.e.,  $O(N)$ , but the second term is at most  $O(\ln N)$ , for large  $N$ , the second term can be safely ignored and we have simply

$$F = -kT \ln Q = F(X^*) \quad (3.11)$$

This is just the maximum-term method for evaluating the partition function [4] and is practically exact for thermodynamically large systems. We thus see that the maximum-term method, or equivalently, the minimization of the constrained free energy  $F(X)$  with respect to the variable  $X$ , is the origin of variational principle in statistical thermodynamics [2]. We will thus use the term variational free energy synonymously with the constrained free energy.

As an illustration of the use of the maximum-term method, we take the energy  $E$  as the macrovariable. Thus we have,

$$Q(X) = \int d\Gamma \delta [E - H(\Gamma)] \exp [-\beta H(\Gamma)] = \Omega(E) e^{-\beta E} \quad (3.12)$$

where  $\Omega(E)$  is the degeneracy, i.e., the microcanonical partition function. The variational free energy is then

$$F(E) = -kT \ln Q(E) = E - kT \ln \Omega(E) \quad (3.13)$$

The variational condition Eq. 3.7 becomes

$$1 - kT \frac{\partial \ln \Omega(E)}{\partial E} = 0 \quad (3.14)$$

i.e.,

$$\frac{\partial \ln \Omega(E)}{\partial E} = \beta \quad (3.15)$$

Note that the left hand side of this equation is the microcanonical definition of  $\beta$  for the system. Thus this variational condition has the simple interpretation that the value of the energy that minimizes the free energy of an isothermal system is such that it results in a temperature of the system that equals the temperature of the thermal bath. This is just the condition for thermal equilibrium!

## 4 The Method of Steepest Descent

While the free energy minimization principle and the maximum-term method are exact, analytical expressions for the exact variational free energy are seldom available. Therefore, in practice variational methods are most often used to construct approximate theories for interacting many-body systems. Two variational methods are widely used in the literature: the method of steepest descent (also called the saddle-point, or stationary-phase method) and the Gibbs-Bogoliubov-Feynman variational bound. We start with the method of steepest descent in this section.

The method of steepest descent is a generalization of Laplace's method [3] introduced in the last section in our discussion of the maximum-term method. We consider the following integral

$$I = \int dx q(x) \exp [-\alpha h(x)] \quad (4.1)$$

where  $x$  is a real variable and  $h(x)$  and  $q(x)$  are analytic functions of  $x$  which may in general be complex, and  $\alpha$  is a large positive parameter. We put a negative sign in the exponential to make apparent the analogy with the Boltzmann weight. Since  $\alpha$

is large, the dominant contribution to the integral comes from the neighborhood of the stationary point of  $h(x)$ . The integration is often extended to the complex plane, in which case the stationary point becomes a saddle point [3]; hence the method is also called the saddle-point method. We will use these two terms interchangeably. For many examples in statistical mechanics, the saddle point occurs for imaginary values of  $x$ . Extending the function  $h(x)$  to  $h(z)$ , and expanding  $h(z)$  about  $z = z^*$  to quadratic order, and performing the resulting Gaussian integral along the steepest-descent direction, we obtain

$$I = \sqrt{\frac{2\pi}{\alpha h^{(2)}(z^*)}} \exp[-\alpha h(z^*)] [q(z^*) + O(\alpha^{-1})] \quad (4.2)$$

where  $h^{(2)}(z^*)$  is the second derivative in the steepest-descent direction [3].

Since we usually work more with the free energy than with the partition function, we define  $f = -\ln I$ .  $f$  is then given by

$$f = \alpha h(z^*) + \frac{1}{2} \ln \frac{\alpha h^{(2)}(z^*)}{2\pi} - \ln q(z^*) + O(\alpha^{-1}) \quad (4.3)$$

If we keep only the leading  $O(\alpha)$  term,  $f$  can be further approximated as

$$f \approx \alpha h(z^*) \quad (4.4)$$

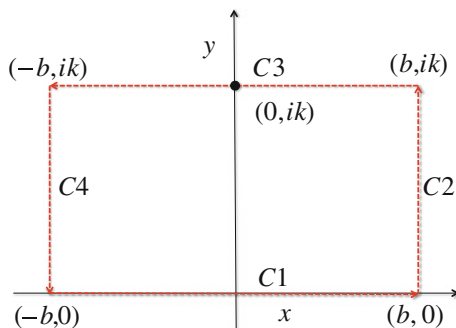
To explain the saddle-point method and illustrate its use, we consider the following integral:

$$I = \int_{-\infty}^{\infty} dx \exp \left[ -\alpha \left( \frac{1}{2} x^2 - ikx \right) \right] \quad (4.5)$$

This integral can, of course, be evaluated exactly by simply completing the square in the exponential, but we use it here to show the key ideas in the saddle-point method. Although the variable  $x$  is real, the integrand is complex, and it is convenient to extend the integration on the real axis to the complex domain  $z$  by using the Cauchy theorem. We note that there is a stationary point at  $z^* = ik$ , which is purely imaginary. This suggests that we make a closed contour as shown in Fig. 2, with the direction of the segments indicated by the red dash arrow. Since there are no residues in the region enclosed by the contour, by the Cauchy theorem we have

$$I_{C1} + I_{C2} + I_{C3} + I_{C4} = 0 \quad (4.6)$$

where  $I_{C1}$  is just the original integral  $I$ . It can be easily shown that the stationary point  $z^* = ik$  is a saddle point: it is a maximum (for the integrand) with respect to variations in  $x$  but a minimum with respect to variations in  $y$ . Thus  $I_{C3}$  runs through the saddle point in the direction of the steepest descent. By taking the limit  $b \rightarrow \infty$ , the integration along  $C2$  and  $C4$  vanish (because of the vanishing of the integrand).



**Fig. 2** Integration contour in the complex plane used to evaluate integral Eq. 4.5. The saddle point is indicated by the *black dot* located at  $(0, ik)$ , and  $b \rightarrow \infty$

We thus have

$$I = -I_{C3} = \int_{-\infty+ik}^{\infty+ik} dz \exp \left[ -\alpha \left( \frac{1}{2}z^2 - ikz \right) \right] \quad (4.7)$$

Completing the square in the exponential, we get

$$I = e^{-\frac{1}{2}\alpha k^2} \int_{-\infty+ik}^{\infty+ik} dz \exp \left[ -\frac{1}{2}\alpha (z - ik)^2 \right] \quad (4.8)$$

Along the C3 contour,  $z = x + ik$ . Thus integrating along  $x$ , i.e., the steepest-descent direction, we obtain

$$I = e^{-\frac{1}{2}\alpha k^2} \int_{-\infty}^{\infty} dx \exp \left[ -\frac{1}{2}\alpha x^2 \right] = \sqrt{\frac{2\pi}{\alpha}} e^{-\frac{1}{2}\alpha k^2} \quad (4.9)$$

As expected, this result is just Eq. 4.2 without the higher-order corrections.

The real power of the saddle-point method, of course, is to evaluate integrals that cannot be performed exactly. As an example, consider the following integral,

$$I = \int_{-\infty}^{\infty} dx \exp [-h(x)] \quad (4.10)$$

with  $h(x) = \frac{1}{2}x^2 - ikx - \lambda(e^{-ix} + e^{ix})$  where  $\lambda > 0$ . We choose this example, because it shares similar mathematical form as the functional integral we introduce in our derivation of the Poisson-Boltzmann equation for the electrolyte solution. Clearly, for nonvanishing values of  $\lambda$ , the integral cannot be evaluated in closed form. We thus obtain an approximate solution using the saddle-point method. Extending the variable to the complex domain, we find the saddle-point condition to be given by

$$z^* = ik + i\lambda(e^{iz^*} - e^{-iz^*}) \quad (4.11)$$

Inspection of this equation suggests that the saddle point is located on the imaginary axis. We thus denote the saddle-point value as  $z^* = iy^*$ , so that the above equation becomes

$$y^* = k - \lambda(e^{y^*} - e^{-y^*}) = k - 2\lambda \sinh y^* \quad (4.12)$$

which yields a real solution for  $y^*$ . (It can be checked that the real solution is unique; this can be done, for example, by graphing the functions on the two sides of the equation.) The value of the function at the saddle point, upon using Eq. 4.12, is

$$h(y^*) = \frac{1}{2}y^{*2} + 2\lambda (y^* \sinh y^* - \cosh y^*) \quad (4.13)$$

It can be easily seen that the steepest-descent direction around the saddle point is in the direction of  $x$ , with a second derivative given by

$$h^{(2)}(y^*) = 1 + 2\lambda \cosh y^* \quad (4.14)$$

The approximate value of the integral is then

$$I \approx \left( \frac{2\pi}{1 + 2\lambda \cosh y^*} \right)^{1/2} \exp \left[ 2\lambda (\cosh y^* - y^* \sinh y^*) - \frac{1}{2}y^{*2} \right] \quad (4.15)$$

## 5 The Gibbs-Bogoliubov-Feynman Variational Principle

We start with the mathematical inequality

$$e^x \geq 1 + x \quad (5.1)$$

for any real number  $x$ . If  $x$  is a stochastic variable, we may write

$$e^x = e^{(x)+x-\langle x \rangle} \geq e^{(x)} (1 + x - \langle x \rangle) \quad (5.2)$$

where the angular brackets denotes the average over the distribution of  $x$ . Taking the average of both sides in the above expression, we get

$$\langle e^x \rangle \geq e^{(x)} \quad (5.3)$$

Now consider the partition function Eq. 3.1. In general, the partition function cannot be evaluated exactly. The idea of the Gibbs-Bogoliubov-Feynman variational method is to evaluate it approximately using a reference Hamiltonian  $H_R(\Gamma)$  for which the partition function can be obtained exactly. Let the partition function for this reference Hamiltonian be  $Q_R$ , so

$$Q_R = \int d\Gamma \exp[-\beta H_R(\Gamma)] \quad (5.4)$$

Next, we write

$$Q = \int d\Gamma \exp[-\beta H_R(\Gamma) - \beta H(\Gamma) + \beta H_R(\Gamma)] \quad (5.5)$$

Multiplying and dividing by  $Q_R$ , and noting

$$\langle A \rangle_R = Q_R^{-1} \int d\Gamma A(\Gamma) \exp[-\beta H_R(\Gamma)] \quad (5.6)$$

where  $A$  is any variable that depends on the microstate  $\Gamma$ , we obtain

$$Q = Q_R \langle \exp[-\beta H + \beta H_R] \rangle_R \geq Q_R \exp[-\beta \langle H \rangle_R + \beta \langle H_R \rangle_R] \quad (5.7)$$

Taking the logarithm and multiplying by  $-kT$ , we obtain

$$F \leq F_R + \langle H \rangle_R - \langle H_R \rangle_R \quad (5.8)$$

where  $F_R$  is the free energy for the reference system. This is the Gibbs-Bogoliubov-Feynman inequality [5–7], which allows to estimate the closest upper bound that can be achieved *for a given choice of the reference system*. Noting further that,

$$F_R = \langle H_R \rangle_R - TS_R \quad (5.9)$$

Equation 5.8 can alternatively be written as

$$F \leq \langle H \rangle_R - TS_R \equiv F_{var} \quad (5.10)$$

Therefore, to best approximate the true free energy  $F$ , we choose a reference Hamiltonian that makes  $F_{var}$  a minimum.

## 6 A Toy Example

In order to illustrate the use of the steepest-descent and GBF methods and compare between the two, we consider the following integral,

$$I = \int_{-\infty}^{\infty} dx \exp[-h(x)] \quad (6.1)$$

in which  $h(x) = \frac{1}{2}\epsilon x^2 + \frac{1}{4!}u x^4 - kx$  is a purely real function with  $u > 0$ . (Note the parameter  $\alpha$  is unnecessary as it can be absorbed by a rescaling of the variable  $x$ .) This function has a similar mathematical form to the  $\phi^4$  field theory widely used in the study of critical phenomena [8], with  $k$  playing the role of the external field. We will be interested in the value of the integral as a function of  $k$  as well as the mean and variance for the variable  $x$ . Without loss of generality we can set  $u = 1$  (this can always be achieved by a redefinition of  $\epsilon$  and  $k$ .) For large and positive  $\epsilon$ , the quartic term is unimportant. As  $\epsilon$  decreases towards zero; the effect of the quartic term becomes more pronounced. Since the integral has the mathematical structure of a partition function, we refer to  $h$  as the ‘‘Hamiltonian’’.

As the function is real with a real minimum, the steepest-descent approximation reduces to the Laplace approximation. The minimum condition is given by

$$\epsilon x^* + \frac{1}{6}x^{*3} = k \quad (6.2)$$

The value of the ‘‘Hamiltonian’’ at the minimum is

$$h(x^*) = -\frac{1}{2}\epsilon x^{*2} - \frac{1}{8}x^{*4} \quad (6.3)$$

The second derivative is given by

$$h^{(2)}(x^*) = \epsilon + \frac{1}{2}x^{*2} \quad (6.4)$$

The approximate value of the ‘‘free energy’’ corresponding to the integral is

$$f = -\ln I \approx -\frac{1}{2}\epsilon x^{*2} - \frac{1}{8}x^{*4} + \frac{1}{2} \ln \frac{\epsilon + \frac{1}{2}x^{*2}}{2\pi} \quad (6.5)$$

As the nonlinear effect is strongest for  $\epsilon = 0$ , we investigate this special case. One easily gets in this case  $x^* = 6^{1/3}k^{1/3}$ , and the ‘‘free energy’’ is then

$$f = -\frac{3}{4}6^{1/3}k^{4/3} + \frac{1}{2} \ln \frac{6^{2/3}k^{2/3}}{4\pi} \quad (6.6)$$

Note that the free energy becomes logarithmically divergent as  $k \rightarrow 0$ , while the original integral is clearly convergent. This is indication of the breaking down of the approximation.

Within the steepest-descent approximation, the average is taken to be the saddle-point value,

$$\langle x \rangle = x^* \quad (6.7)$$

(upon ignoring higher-order corrections in an expansion in  $\alpha^{-1}$ ; see Eqs. 4.1–4.4), and the variance of  $x$  is given by

$$\langle(\Delta x)^2\rangle = \frac{1}{h^{(2)}(x^*)} \quad (6.8)$$

which follows from the use of linear response theory

$$\langle(\Delta x)^2\rangle = \frac{\partial\langle x\rangle}{\partial k} \quad (6.9)$$

We now evaluate the integral Eq. 6.1 using the GBF bound. To this end, we introduce a two-parameter reference “Hamiltonian”,

$$h_R = \frac{1}{2}a(x - x^*)^2 \quad (6.10)$$

where  $x^*$  and  $a$  are the variational parameters. The GBF bound now reads:

$$f = -\ln I \leq f_R + \langle h\rangle_R - \langle h_R\rangle_R \quad (6.11)$$

where the average  $\langle\cdots\rangle_R$  here means

$$\langle\cdots\rangle_R = \left(\frac{a}{2\pi}\right)^{1/2} \int_{-\infty}^{\infty} dx (\cdots) \exp\left[-\frac{1}{2}a(x - x^*)^2\right] \quad (6.12)$$

For the reference “Hamiltonian” Eq. 6.10, one easily finds

$$\langle h_R\rangle_R = \frac{1}{2} \quad (6.13)$$

$$f_R = \frac{1}{2} \ln\left(\frac{a}{2\pi}\right) \quad (6.14)$$

$$\langle h\rangle_R = \frac{1}{2}\epsilon x^{*2} + \frac{1}{2}\epsilon a^{-1} + \frac{1}{4!}\left(x^{*4} + 6a^{-1}x^{*2} + 3a^{-2}\right) - kx^* \quad (6.15)$$

The parameters  $x^*$  and  $a$  are obtained by minimization of the right hand side of Eq. 6.11 using Eqs. 6.13–6.15, yielding, respectively

$$\epsilon x^* + \frac{1}{3!}x^{*3} + \frac{1}{2}a^{-1}x^* - k = 0 \quad (6.16)$$

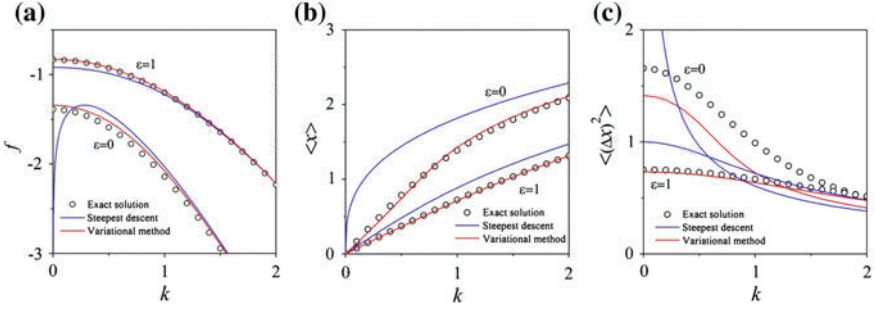
and

$$2a^2 - 2\epsilon a - ax^{*2} - 1 = 0 \quad (6.17)$$

The positive root of Eq. 6.17 is given by

$$a = \frac{1}{4} \left[ 2\epsilon + x^{*2} + \sqrt{8 + (2\epsilon + x^{*2})^2} \right] \quad (6.18)$$





**Fig. 3** Results obtained from the steepest-descent method (blue curve) and the GBF variational method (red curve), compared to the exact numerical results (black circles), for the example given by Eq. 6.1. From left to right the “free energy”, the mean, and the variance

The minimized “free energy” after simplification using Eqs. 6.16 and 6.17 is:

$$f = \frac{1}{2} \ln \left( \frac{a}{2\pi} \right) - \frac{1}{4} + \frac{1}{4} \epsilon a^{-1} - \frac{1}{2} \epsilon x^{*2} - \frac{1}{8} x^{*4} - \frac{3}{8} a^{-1} x^{*2} \quad (6.19)$$

By the Gaussian ansatz, the mean and variance are given respectively by

$$\langle x \rangle = x^* \quad (6.20)$$

$$\langle (\Delta x)^2 \rangle = a^{-1} \quad (6.21)$$

In Fig. 3, we plot the “free energy”, the mean and the variance as a function of  $k$  for two values of the parameter  $\epsilon$ . For comparison, we include the results from the steepest-descent method (blue curve), from the GBF method (red curve), and from exact numerical solution (black circles). In all cases, the variational method provides a far closer agreement with the numerical results than the simple steepest descent. For the mean, which in essence is an equation of state, the agreement is excellent even for  $\epsilon = 0$ , and very good agreement is also obtained for the “free energy” under the “worst” condition  $\epsilon = 0$  and  $k = 0$ . Note also that the GBF variational free energy is always higher than the true free energy, though no such restrictions apply for the steepest-descent method. The result for the fluctuation from the GBF method is quite good for  $\epsilon = 1$ ; it is less accurate quantitatively for  $\epsilon = 0$ , but still captures the qualitative behavior. In contrast, the steepest-descent method yields qualitatively incorrect behavior for  $\epsilon = 0$ . Finally we note that both approximations become increasingly more accurate at large  $k$  and/or  $\epsilon$ .

Those who are familiar with the statistical field theory will recognize the steepest-descent and the GBF treatments as the respective analogue of the random-phase approximation (RPA) [9, 10] and the self-consistent Hartree approximation [11]. (We note, however, that the term RPA has different meanings in the different communities. For example, in liquid-state theory, it usually refers to approximating the

direct correlation function by the pair interaction potential in the closure for the Ornstein-Zernike equation [12]. In many-body and condensed matter physics, RPA is considered synonymous with the self-consistent Hartree approximation [13]. In this chapter, we will use the term RPA to refer to a simple Gaussian approximation around the saddle-point, or equivalently, linear response by perturbation around the saddle-point [9, 10].)

## 7 Mean-Field Solution for the Interacting Ising Model

The Ising model is the best known model for a wide range of phase transitions, including ferromagnetism, liquid-vapor transition, and phase separation in binary mixtures. In its most common form, the model consists of  $N$  “spins” on a lattice with coordination number  $z$  in an external field  $h$ . Each spin can be either in an up or down state, which is denoted by the spin variable  $s_i = \pm 1$  with  $+$  for the up state and  $-$  for the down state. The spins interact with each other through nearest neighbor pairs in such a way as to favor the same orientation. The Hamiltonian for the system is

$$H = -\frac{1}{2}J \sum_{i,j}' s_i s_j - \sum_i h_i s_i \quad (7.1)$$

where  $J > 0$  is the coupling constant,  $h_i$  is the external field, here allowed to be spatially dependent for generality, and the prime on the first sum restricts  $i$  and  $j$  to be nearest neighbors of each other. Henceforth, to economize notation, we set the energy unit to be  $kT$  and the entropy unit to be  $k$ .

The partition function of the system is then

$$Z = \sum_{\{s\}} \exp(-H) \quad (7.2)$$

where  $\{s\}$  is a collective notation for all the spin states. It can be easily shown [4] that the model can be applied to describe a lattice-gas fluid in a grand canonical ensemble by introducing the occupation variable  $\sigma = (1 + s)/2$  and identifying the nearest-neighbor attraction energy  $\epsilon = -4J$  and chemical potential  $\mu = -4Jz + 2h$ .

The mean-field solution of the Ising model in typical textbooks is usually derived using a Braggs-William random mixing approximation [4], which amounts to ignoring the correlations due to interaction and treating the distribution of the spins as completely random. Alternatively, one may invoke a local self-consistent field argument by replacing the local instantaneous field at location  $i$ ,  $h_i + J \sum_j' s_j$  with the average  $h_i + J \sum_j' m_j$  where  $m_i$  is the average of  $s_i$ . The local average of  $m_i$  is in turn obtained through the self-consistency condition

$$m_i = \frac{\sum_{s_i} s_i \exp \left[ (h_i + J \sum_j' m_j) s_i \right]}{\sum_{s_i} \exp \left[ (h_i + J \sum_j' m_j) s_i \right]} = \tanh(h_i + J \sum_j' m_j) \quad (7.3)$$

For spatially uniform system,  $m_i = m$ , and the above equation simplifies to:

$$m = \tanh(h + Jzm) \quad (7.4)$$

where  $z$  is the lattice coordination number. This is the well-known mean-field equation of state relating the magnetization per spin to the external field. From Eq. 7.4, we find the familiar mean-field critical point at  $h_c = 0$  and  $J_c z = 1$

We now derive the mean-field solution using a variational approach. We make the reference Hamiltonian an effective non-interacting one, with spins in an effective one-body field  $h_{i,R}$

$$H_R = - \sum_i h_{i,R} s_i \quad (7.5)$$

The partition function for  $H_R$  can be trivially worked out to be

$$Z_R = 2^N \prod_i \cosh(h_{i,R}) \quad (7.6)$$

from which we obtain the free energy of the reference system

$$F_R = - \sum_i \ln \cosh(h_{i,R}) - N \ln 2 \quad (7.7)$$

$\langle H \rangle_R$  and  $\langle H_R \rangle_R$  can be straightforwardly evaluated to be

$$\langle H \rangle_R = -\frac{1}{2} J \sum_{i,j} m_i m_j - \sum_i h_i m_i \quad (7.8)$$

and

$$\langle H_R \rangle_R = - \sum_i h_{i,R} m_i \quad (7.9)$$

where  $m_i$  is given by

$$m_i = \langle s_i \rangle_R = - \frac{\partial F_R}{\partial h_{i,R}} = \tanh(h_{i,R}) \quad (7.10)$$

The variational free energy  $F[h_{i,R}]$  is obtained by combining Eqs. 7.7–7.9, and the effective field  $h_{i,R}$  is obtained from

$$\frac{\partial F}{\partial h_{i,R}} = 0 \quad (7.11)$$

which, along with Eq. 7.10, gives

$$h_{i,R} = h_i + J \sum_j' m_j \quad (7.12)$$

Substituting this back in Eq. 7.10, we obtain the self-consistent Eq. 7.3.

Although  $m_i$  is defined through Eq. 7.10, it can be shown that within the variational free energy framework, it is just the average of the spin variable at  $i$ . To demonstrate this, we start with

$$\langle s_i \rangle = - \frac{\partial F}{\partial h_i} \quad (7.13)$$

By construction, the only place where  $h_i$  enters directly in the variational free energy is through  $\langle H \rangle_R$ . Furthermore, the dependence of  $h_{i,R}$  on  $h_i$  does not contribute because of the variational condition Eq. 7.11. We thus have

$$\langle s_i \rangle = - \frac{\partial \langle H \rangle_R}{\partial h_i} = m_i \equiv \langle s_i \rangle_R \quad (7.14)$$

This conclusion that the ensemble average is equal to the average in the reference system is a general one within the variational approximation.

The variational condition Eq. 7.11 can alternatively be cast in a different form by directly using the local magnetization  $m_i$ . Since Eq. 7.10 establishes a one-to-one monotonic relationship between the variational parameter  $h_{i,R}$  and  $m_i$ , we may use  $m_i$  itself as the variational parameter. Because the reference system consists of uncoupled spins, each having two states, its entropy is simply

$$S_R = - \sum_i [p(s_i = 1) \ln p(s_i = 1) + p(s_i = -1) \ln p(s_i = -1)] \quad (7.15)$$

Noting that  $m_i = p(s_i = 1) - p(s_i = -1) = 2p(s_i = 1) - 1$ , the above equation can be written as

$$\begin{aligned} S_R &= - \sum_i \left[ \frac{1+m_i}{2} \ln \frac{1+m_i}{2} + \frac{1-m_i}{2} \ln \frac{1-m_i}{2} \right] \\ &= N \ln 2 - \frac{1}{2} \sum_i [(1+m_i) \ln(1+m_i) + (1-m_i) \ln(1-m_i)] \end{aligned} \quad (7.16)$$

where  $N$  is the total number of spins.  $N \ln 2$  in the second line is simply the entropy of a completely unbiased system of  $N$  independent spins, whereas the remaining terms account for the decrease in entropy due to ordering.

With Eq. 7.16, the variational free energy is

$$F_{var} = -\frac{1}{2}J \sum'_{i,j} m_i m_j - \sum_i h_i m_i + \frac{1}{2} \sum_i [(1 + m_i) \ln(1 + m_i) + (1 - m_i) \ln(1 - m_i)] - N \ln 2 \quad (7.17)$$

The minimized free energy is obtained from the variational condition

$$\frac{\partial F_{var}}{\partial m_i} = 0 \quad (7.18)$$

which yields the mean-field equation of state, Eq. 7.10.

The variational free energy can be more systematically obtained using a combination of the identity transformation and the saddle-point method. To this end, we insert the identity  $\int dm_i \delta(m_i - s_i)$  for each spin, to write the Boltzmann weight  $\exp(-H)$  as

$$\begin{aligned} \exp[-H(\{s_i\})] &= \int \prod_i dm_i \delta(m_i - s_i) \exp[-H(\{m_i\})] \\ &= \frac{1}{(2\pi)^N} \int \prod_i dm_i d\lambda_i \exp \left[ -H(\{m_i\}) + i \sum_i \lambda_i (m_i - s_i) \right] \end{aligned} \quad (7.19)$$

where the second line follows from making use of the Fourier representation of the delta function:

$$\delta(m_i - s_i) = \frac{1}{2\pi} \int d\lambda_i \exp[i\lambda_i (m_i - s_i)] \quad (7.20)$$

The identity transformation has turned the problem of interacting spins into one of independent spins in fluctuating “external” field  $i\lambda$ . The summation over the spin variable  $s_i$  can now be performed trivially to yield the partition function

$$Z = \frac{1}{(2\pi)^N} \int \prod_i dm_i d\lambda_i \exp \left[ -H(\{m_i\}) + i \sum_i \lambda_i m_i + \sum_i \ln \cosh(i\lambda_i) \right] \quad (7.21)$$

We now make the saddle-point approximation on this multidimensional integral, by taking the stationary point of the exponent with respect to  $m_i$  and  $\lambda_i$ ; this yields,

$$i\lambda_i = \frac{\partial H}{\partial m_i} = -J \sum'_j m_j - h_i \quad (7.22)$$

and

$$im_i = -i \tanh(i\lambda_i) \quad (7.23)$$

respectively. Clearly from Eq. 7.22, the saddle point lies on the imaginary axis of  $\lambda$ , so we denote the saddle-point value of  $\lambda$  as  $\lambda^* = i\eta$ , and the above equations become

$$\eta_i = J \sum_j m_j + h_i \quad (7.24)$$

and

$$m_i = \tanh \eta_i \quad (7.25)$$

which are the same as Eqs. 7.10 and 7.12, with the identification  $\eta_i = h_{i,R}$

A closer examination of Eq. 7.21 reveals that the three terms in the exponent correspond respectively to the  $\langle H \rangle_R$ ,  $\langle H_R \rangle_R$  and  $F_R$  terms in the GBF variational approach. This is no accident, because the identity transformation essentially turns the problem of interacting spins into one of independent spins in an effective fluctuating field, and the saddle-point condition is the condition for finding the optimal value for the effective field.

## 8 The Poisson-Boltzmann Equation

The Poisson-Boltzmann equation is a mean-field equation for the mean-electrostatic potential generated by some fixed external charge distribution in the presence of small mobile ions. The mobile ions are treated as point particles whose spatial distribution is given by the Boltzmann weight with the energy being the electrostatic energy of an ion in the mean electrostatic potential. To simplify notation, we scale the energy by  $kT$ , charge by the elementary charge  $e$ , and define a dimensionless permittivity  $\epsilon = \epsilon_r \epsilon_0 kT / e^2$ , where  $\epsilon_0$  is the vacuum permittivity and  $\epsilon_r$  the dielectric constant (allowed to be spatially dependent). For simplicity, we consider the electrolyte to be a monovalent 1:1 salt. The mean electrostatic potential  $\psi$  in the presence of a fixed external charge distribution  $\rho_{ex}$  is then described by

$$-\nabla \cdot (\epsilon \nabla \psi) = \rho_{ex} - 2c^b \sinh \psi \quad (8.1)$$

where  $c^b$  is the bulk salt concentration and the electrostatic potential is defined such that  $\psi = 0$  in the bulk far away from the fixed charge.

While the Poisson-Boltzmann equation can be constructed quite intuitively by combining the Poisson equation for electrostatics with the Boltzmann distribution for the small mobile ions, which are treated as ideal gas particles in the electrostatic potential, here we derive it using variational approaches. The systematic derivation is necessary for calculating the free energy of the system. We first provide a simple, thermodynamic derivation and then a more systematic one using field theoretical techniques.