20

VARIATIONAL PROPERTIES, PERTURBATION EXPANSIONS, AND MEAN FIELD THEORY

20-1 THE BOGOLIUBOV VARIATIONAL THEOREM

To calculate the fundamental equation for a particular system we must first evaluate the permissible energy levels of the system and then, given those energies, we must sum the partition sum. Neither of these steps is simple, except for a few "textbook models." In such models, several of which we have studied in preceding chapters, the energy eigenvalues follow a simple sequence and the partition sum is an infinite series that can be summed analytically. But for most systems both the enumeration of the energy eigenvalues and the summation of the partition sum pose immense computational burdens. Approximation techniques are required to make the calculations practical. In addition these approximation techniques provide important heuristic insights to complex systems.

The strategy followed in the approximation techniques to be described is first to identify a soluble model that is somewhat similar to the model of interest, and then to apply a method of controlled corrections to calculate the effect of the difference in the two models. Such an approach is a statistical "perturbation method."

Because perturbation methods rest upon the existence of a library of soluble models, there is great stress in the statistical mechanical literature on the invention of new soluble models. Few of these have direct physical relevance, as they generally are devised to exploit some ingenious mathematical trick of solution rather than to mirror real systems (thereby giving rise to the rather abstract flavor of some statistical mechanical literature).

The first step in the approximation strategy is to identify a practical criterion for the choice of a soluble model with which to approximate a given system. That criterion is most powerfully formulated in terms of the Bogoliubov variational theorem.

Consider a system with a Hamiltonian $\mathscr{H}$, and a soluble model system with a Hamiltonian $\mathscr{H}_0$. Let the difference be $\mathscr{H}_1$, so that $\mathscr{H} = \mathscr{H}_0 + \mathscr{H}_1$. It is then convenient to define

$$\mathscr{H}(\lambda) = \mathscr{H}_0 + \lambda \mathscr{H}_1 \tag{20.1}$$

where λ is a parameter inserted for analytic convenience. By permitting λ to vary from zero to unity we can smoothly bridge the transition from the soluble model system ($\mathscr{H}_0$) to the system of interest; $\mathscr{H}(1) = \mathscr{H}_0 + \mathscr{H}_1$.

The Helmholtz potential corresponding to $\mathscr{H}(\lambda)$ is $F(\lambda)$, where

$$-\beta F(\lambda) = \ln \sum_j e^{-\beta E_j(\lambda)} \equiv \ln \operatorname{tr} e^{-\beta \mathscr{H}(\lambda)} \tag{20.2}$$

Here the symbol $\operatorname{tr} e^{-\beta \mathscr{H}(\lambda)}$ (to be read as the "trace" of $e^{-\beta \mathscr{H}(\lambda)}$) is *defined* by the second equality; *the trace of any quantity is the sum of its quantum eigenvalues*. We use the notation "tr" simply as a convenience.

We now study the dependence of the Helmholtz potential on λ. The first derivative is[1]

$$\frac{dF(\lambda)}{d\lambda} = \frac{\operatorname{tr} \mathscr{H}_1 e^{-\beta(\mathscr{H}_0 + \lambda \mathscr{H}_1)}}{\operatorname{tr} e^{-\beta(\mathscr{H}_0 + \lambda \mathscr{H}_1)}} = \langle \mathscr{H}_1 \rangle \tag{20.3}$$

and the second derivative is

$$\frac{d^2 F}{d\lambda^2} = -\beta \left[\frac{\operatorname{Tr} \mathscr{H}_1^{\,2} e^{-\beta(\mathscr{H}_0 + \lambda \mathscr{H}_1)}}{\operatorname{tr} e^{-\beta(\mathscr{H}_0 + \lambda \mathscr{H}_1)}} - \left(\frac{\operatorname{tr} \mathscr{H}_1 e^{-\beta(\mathscr{H}_0 + \lambda \mathscr{H}_1)}}{\operatorname{tr} e^{-\beta(\mathscr{H}_0 + \lambda \mathscr{H}_1)}} \right)^2 \right] \tag{20.4}$$

$$= -\beta \left[\langle \mathscr{H}_1^2 \rangle - \langle \mathscr{H}_1 \rangle^2 \right] \tag{20.5}$$

$$= -\beta \langle \mathscr{H}_1 - \langle \mathscr{H}_1 \rangle \rangle^2 \tag{20.6}$$

where the averages are taken with respect to the canonical weighting factor $e^{-\beta \mathscr{H}(\lambda)}$. The operational meaning of these weighted averages will be clarified by a specific example to follow.

An immediate and fateful consequence of equation 20.6 is that $d^2F/d\lambda^2$ is negative (or zero) for all λ

$$\frac{d^2 F}{d\lambda^2} \le 0 \qquad \text{(for all } \lambda\text{)} \tag{20.7}$$

---

[1] In the quantum mechanical context the operators $\mathscr{H}_0$ and $\mathscr{H}_1$ are here assumed to commute. The result is independent of this assumption. For the noncommutative case, and for an elegant general discussion see R. Feynman, *Statistical Mechanics—A Set of Lectures* (W. A. Benjamin, Inc., Reading, Massachusetts, 1972).

Consequently a plot of $F(\lambda)$ as a function of λ is everywhere concave. It follows that $F(\lambda)$ lies below the straight line tangent to $F(\lambda)$ at $\lambda = 0$;

$$F(\lambda) \leq F(0) + \lambda (dF/d\lambda)_{\lambda=0} \tag{20.8}$$

and specifically, taking $\lambda = 1$

$$F \leq F_0 + \langle \mathscr{H}_1 \rangle_0 \tag{20.9}$$

The quantity $\langle \mathscr{H}_1 \rangle_0$ is as defined in equation 20.3, but with $\lambda = 0$; it is the average value of $\mathscr{H}_1$ in the soluble model system. Equation 20.9 is the Bogoliubov inequality. It states that *the Helmholtz potential of a system with Hamiltonian* $\mathscr{H} = \mathscr{H}_0 + \mathscr{H}_1$ *is less than or equal to the "unperturbed" Helmholtz potential* (corresponding to $\mathscr{H}_0$) *plus the average value of the "perturbation"* $\mathscr{H}_1$ *as calculated in the unperturbed (or soluble model) system.*

Because the quantity on the right of equation 20.9 is an upper bound to the Helmholtz potential of the ("perturbed") system, it clearly is desirable that this bound be as small as possible. Consequently *any adjustable parameters in the unperturbed system are best chosen so as to minimize the quantity* $F_0 + \langle \mathscr{H}_1 \rangle_0$.

This is the criterion for the choice of the "best" soluble model system. Then F_0 is the Helmholtz potential of the optimum model system, and $\langle \mathscr{H}_1 \rangle_0$ is the leading correction to this Helmholtz potential.

The meaning and the application of this theorem are best illustrated by a specific example, to which we shall turn momentarily. However we first recast the Bogoliubov inequality in an alternative form that provides an important insight. If we write F_0, the Helmholtz potential of the unperturbed system, explicitly as

$$F_0 = \langle \mathscr{H}_0 \rangle_0 - TS_0 \tag{20.10}$$

then equation 20.9 becomes

$$F \leq \langle \mathscr{H}_0 \rangle_0 + \langle \mathscr{H}_1 \rangle_0 - TS_0 \tag{20.11}$$

or

$$F \leq \langle \mathscr{H} \rangle_0 - TS_0 \tag{20.12}$$

That is, *the Helmholtz potential of a system with Hamiltonian* $\mathscr{H} = \mathscr{H}_0 + \mathscr{H}_1$ *is less than or equal to the full energy* $\mathscr{H}$ *averaged over the state probabilities of the unperturbed system, minus the product of T and the entropy of the unperturbed system.*

Example 1

A particle of mass m is constrained to move in one dimension in a quartic potential of the form $V(x) = D(x/a)^4$, where $D > 0$ and where a is a measure of the linear extension of the potential. The system of interest is composed of $\tilde{N}$ such particles in thermal contact with a reservoir of temperature T. An extensive parameter of the system is defined by $X \equiv \tilde{N}a$, and the associated intensive parameter is denoted by P. Calculate the equations of state $U = U(T, X, \tilde{N})$ and $P = P(T, X, \tilde{N})$, and the heat capacity $c_p(T, X, \tilde{N})$.

To solve this problem by the standard algorithm would require first a quantum mechanical calculation of the allowed energies of a particle in a quartic potential, and then summation of the partition sum. Neither of these calculations is analytically tractable. We avoid these difficulties by seeking an approximate solution. In particular we inquire as to the best quadratic potential (i.e., the best simple harmonic oscillator model) with which to approximate the system, and we then assess the leading correction to account for the difference in the two models.

The quadratic potential that, together with the kinetic energy, defines the "unperturbed Hamiltonian" is

$$V_0(x) = \tfrac{1}{2} m\omega_0^2 x^2 \tag{a}$$

where ω_0 is an as-yet-unspecified constant. Then the "perturbing potential," or the difference between the true Hamiltonian and that of the soluble model system, is

$$\mathscr{H}_1 = D\left(\frac{x}{a}\right)^4 - \frac{1}{2} m\omega_0^2 x^2 \tag{b}$$

The Helmholtz potential of the harmonic oscillator model system is (recall equations 16.22 to 16.24)[2]

$$F_0 = -\tilde{N} k_B T \ln z_0 = \tilde{N}\beta^{-1} \ln\left(e^{\beta\hbar\omega_0/2} - e^{-\beta\hbar\omega_0/2}\right) \tag{c}$$

and the Bogoliubov inequality states that

$$F \le \tilde{N}\beta^{-1} \ln\left(e^{\beta\hbar\omega_0/2} - e^{-\beta\hbar\omega_0/2}\right) + \tilde{N} D\left\langle\left(\frac{x}{a}\right)^4\right\rangle_0 - \left(\frac{\tilde{N}}{2}\right) m\omega_0^2 \langle x^2\rangle_0 \tag{d}$$

Before we can draw conclusions from this result we must evaluate the second and third terms. It is an elementary result of mechanics (the "virial theorem") that the value of the potential energy $(\frac{1}{2} m\omega_0^2 x^2)$ in the nth state of a harmonic oscillator is one half the total energy, so that

$$\left(\tfrac{1}{2} m\omega_0^2 x^2\right)_{n\text{th state}} = \tfrac{1}{2}\left(n + \tfrac{1}{2}\right)\hbar\omega_0 \tag{e}$$

---

[2] But note that the zero of energy has been shifted by $\hbar\omega_0/2$, the so-called zero point energy. The allowed energies are $(n + \frac{1}{2})\hbar\omega_0$.

and a similar quantum mechanical calculation gives

$$\langle x^4 \rangle_{n\text{th state}} = \left(\frac{3\hbar^2}{2m^2\omega_0^2} \right) \left(n^2 + n + \frac{1}{2} \right) \tag{f}$$

With the values of these quantities in the nth state we must now average over all states n. Averaging equation (e) in the unperturbed system

$$\left\langle \frac{1}{2} m\omega_0^2 x^2 \right\rangle_0 = \frac{1}{2}\left[\langle n \rangle + \frac{1}{2} \right] \hbar\omega_0 = \frac{1}{2} U_0 = \frac{1}{4}\hbar\omega_0 \frac{e^{\beta\hbar\omega_0} + 1}{e^{\beta\hbar\omega_0} - 1} \tag{g}$$

and we also find

$$\frac{D}{a^4} \langle x^4 \rangle_0 = \frac{D}{a^4} \frac{3\hbar^2}{2m^2\omega_0^2} \left[\langle n^2 \rangle + \frac{U}{\hbar\omega_0} \right]$$

$$= \frac{D}{a^4} \frac{3\hbar^2}{2m^2\omega_0^2} \left[\frac{e^{\beta\hbar\omega_0} + 1}{(e^{\beta\hbar\omega_0} - 1)^2} + \frac{e^{\beta\hbar\omega_0} + 1}{2(e^{\beta\hbar\omega_0} - 1)} \right]$$

$$= \frac{3D\hbar^2}{4a^4 m^2 \omega_0^2} \left(\frac{e^{\beta\hbar\omega_0} + 1}{e^{\beta\hbar\omega_0} - 1} \right)^2 \tag{h}$$

Inserting these last two results (equations g and h) into the Bogoliubov inequality (equation d)

$$F \leq \tilde{N}\beta^{-1} \ln\left(e^{\beta\hbar\omega_0/2} - e^{-\beta\hbar\omega_0/2} \right)$$

$$+ \frac{3\tilde{N}D\hbar^2}{4a^4 m^2\omega_0^2} \left(\frac{e^{\beta\hbar\omega_0} + 1}{e^{\beta\hbar\omega_0} - 1} \right)^2 - \frac{1}{2}\tilde{N}\hbar\omega_0 \frac{e^{\beta\hbar\omega_0} + 1}{e^{\beta\hbar\omega_0} - 1} \tag{i}$$

The first term is the Helmholtz potential of the unperturbed harmonic oscillator system, and the two remaining terms are the leading correction. The inequality states that the sum of all higher-order corrections would be positive, so that the right-hand side of equation (i) is an upper bound to the Helmholtz potential.

The frequency ω_0 of the harmonic oscillator system has not yet been chosen. Clearly the best approximation is obtained by making the upper bound on F as small as possible. Thus *we choose* ω_0 *so as to minimize the right-hand side of equation i, which then becomes the best available approximation to the Helmholtz potential of the system.* Denote the value of ω_0 that minimizes F by $\tilde{\omega}_0$ (a function of T, X $(= \tilde{N}a)$, and $\tilde{N}$). Then ω_0 in equation (i) can be replaced by $\tilde{\omega}_0$ and the "less than or equal" sign $(\leq)$ can be replaced by an "approximately equal" sign $(\simeq)$. So interpreted, equation (i) is the (approximate) fundamental equation of the system.

The mechanical equation of state is, then,

$$-\frac{P}{T}=\frac{1}{\tilde{N}}\left(\frac{\partial F}{\partial a}\right)_{T,\tilde{N}}=\frac{1}{\tilde{N}}\left(\frac{\partial F}{\partial a}\right)_{T,\tilde{N},\tilde{\omega}_0}+\frac{1}{\tilde{N}}\left(\frac{\partial F}{\partial \tilde{\omega}_0}\right)_{T,\tilde{N},a}\left(\frac{\partial \tilde{\omega}_0}{\partial a}\right)_{T,\tilde{N}} \tag{j}$$

At this point the algebra becomes cumbersome, though straightforward in principle. The remaining quantities sought for can be found in similar form. Instead we turn our attention to a simpler version of the same problem.

Example 2

We repeat the preceding Example, but we consider the case in which the coefficient D/a^4 is small (in a sense to be made more quantitative later), permitting the use of classical statistics. Furthermore we now choose a square-well potential as the unperturbed potential

$$V_0(x)=\begin{cases}0 & \text{if } -\dfrac{L}{2}<x<\dfrac{L}{2}\\[2ex] \infty & \text{if } |x|>\dfrac{L}{2}\end{cases}$$

The optimum value of L is to be determined by the Bogoliubov criterion.

The unperturbed Helmholtz potential is determined by

$$e^{-\beta F_0}=\operatorname{tr} e^{-\beta\mathscr{H}_0}=\iint\frac{dx\,dp_x}{h}e^{-\beta[p_x^2/2m+V_0(x)]}$$

$$=\frac{1}{h}\int_{-L/2}^{L/2}dx\int_{-\infty}^{\infty}dp_x\,e^{-\beta p_x^2/2m}$$

$$=\frac{1}{h}(2\pi mk_BT)^{1/2}L$$

We have here used classical statistics (as in Sections 16.8 and 16.9), tentatively assuming that L and T are each sufficiently large that k_BT is large compared to the energy differences between quantum states.

The quantity $\langle\mathscr{H}_1\rangle_0$ is, then,

$$\langle\mathscr{H}_1\rangle_0=\frac{\operatorname{tr}\left[Da^{-4}x^4-V_0(x)\right]e^{-\beta\mathscr{H}_0}}{\operatorname{tr}e^{-\beta\mathscr{H}_0}}$$

Furthermore $V_0(x)=0$ for $|x|<L/2$, whereas $e^{-\beta\mathscr{H}_0}=0$ for $|x|>L/2$, so that the term involving $V_0(x)$ vanishes. Then

$$\langle\mathscr{H}_1\rangle_0=\frac{D}{a^4}\langle x^4\rangle_0=\frac{D}{a^4L}\int_{-L/2}^{L/2}x^4\,dx=\frac{D}{80}\left(\frac{L}{a}\right)^4$$

The Bogoliubov inequality now becomes

$$F \leq -k_B T \ln\left[\frac{1}{h}(2\pi m k_B T)^{1/2} L\right] + \frac{1}{80} D\left(\frac{L}{a}\right)^4$$

Minimizing with respect to L

$$L/a = [20 k_B T/D]^{1/4}$$

This result determines the optimum size of a square-well potential with which to approximate the thermal properties of the system, and it determines the corresponding approximate Helmholtz potential.

Finally we return to the criterion for the use of classical statistics. In Section 16.6 we saw that the energy separation of translational states is of the order of $h^2/2mL^2$, and the criterion of classical statistics is that $k_B T \gg h^2/2mL^2$. In terms of D the analogous criterion is

$$\frac{D}{a^4} \lesssim 20 m^2 \frac{(k_B T)^3}{\hbar^4}$$

For larger values of D the procedure would be similar in principle, but the calculation would require summations over the discrete quantum states rather than simple phase-space integration.

Finally we note that if the temperature is high enough to permit the use of classical statistics the original quartic potential problem is itself soluble! Then there is no need to approximate the quartic potential by utilizing a variational theorem. It is left to the reader (Problem 20.1-2) to solve the original quartic potential problem in the classical domain, and to compare that solution with the approximate solution obtained here.

PROBLEMS

20.1-1. Derive equation (h) of Example 1, first showing that for a harmonic oscillator

$$\langle n \rangle = -\frac{1}{z'}\frac{\partial z'}{\partial(\beta\hbar\omega_0)}$$

and

$$\langle n^2 \rangle = \frac{1}{z'}\frac{\partial^2 z'}{\partial(\beta\hbar\omega_0)^2}$$

where

$$z' = e^{\beta\hbar\omega_0/2} z = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega_0 n}$$

20.1-2. Solve the quartic potential problem of Example 2 assuming the temperature to be sufficiently high that classical statistics can be applied. Compare the Helmholtz potential with that calculated in Example 2 by the variational theorem.

20.1-3. Complete Example 2 by writing the Helmholtz potential $F(T, a)$ explicitly. Calculate the "tension" $\mathscr{T}$ conjugate to the "length" a. Calculate the compliance coefficient $a^{-1}(\partial a/\partial \mathscr{T})_T$.

20.1-4. Consider a particle in a quadratic potential $V(x) = Ax^2/2a^2$. Despite the fact that this problem is analytically solvable, approximate the problem by a square potential. Assume the temperature to be sufficiently high that classical statistics can be used in solving the square potential. Calculate the "tension" $\mathscr{T}$ and the compliance coefficient $a^{-1}(\partial a/\partial \mathscr{T})_T$.

20-2 MEAN FIELD THEORY

The most important application of statistical perturbation theory is that in which a system of interacting particles is approximated by a system of noninteracting particles. The optimum noninteracting model system is chosen in accordance with the Bogoliubov inequality, which also yields the first-order correction to the noninteracting or "unperturbed" Helmholtz potential. Because very few interacting systems are soluble analytically, and because virtually all physical systems consist of interacting particles, the "mean field theory" described here is the basic tool of practical statistical mechanics.

It is important to note immediately that the term *mean field theory* often is used in a less specific way. Some of the results of the procedure can be obtained by other more ad hoc methods. Landau-type theories (recall Section 11.4) obtain a temperature dependence of the order parameter that is identical to that obtained by statistical mean field theory. Another approximation, known as the "random phase approximation," also predicts the same equation of state. Neither of these provides a full thermodynamic fundamental equation. Nevertheless various such approximations are referred to generically as mean field theories. We use the term in the more restrictive sense.

Certainly the simplest model of interacting systems, and one that has played a key role in the development of the theory of interacting systems, is the "two-state nearest-neighbor Ising model." The model consists of a regular crystalline array of particles, each of which can exist in either of two orbital states, designated as the "up" and "down" states. Thus the states of the particles can be visualized in terms of classical spins, each of which is permitted only to be either up or down; a site variable σ_j takes the value $\sigma_j = +1$ if the spin at site j is up or $\sigma_j = -1$ if the spin at site j is down. The energies of the two states are $-B$ and $+B$ for the up and down states respectively. In addition nearest neighbor spins have an interaction energy $-2J$ if they are both up or both down, or of $+2J$ if one spin is up and one spin is down. Thus the Hamiltonian is

$$\mathscr{H} = -\sum_{i,j} J_{ij}\sigma_i\sigma_j - B\sum_j \sigma_j \tag{20.13}$$

where $J_{ij} = 0$ if i and j are not nearest neighbors, whereas $J_{ij} = J$ if i and j are nearest neighbors. It should be noted that a specific pair of neighbors (say spins #5 and #8) appears twice in the sum ($i = 5$, $j = 8$ and $i = 8$, $j = 5$).

Quite evidently the problem is an insoluble many-body problem, for each spin is coupled indirectly to every other spin in the lattice. An approximation scheme is needed, and we invoke the Bogoliubov inequality. A plausible form of the soluble model system is suggested by focussing on only the jth spin in the Hamiltonian (20.13); the Hamiltonian is then simply linear in σ_j. We correspondingly choose the "unperturbed" model Hamiltonian to be

$$\mathscr{H}_0 = -\sum_j \hat{B}_j\sigma_j - B\sum_j \sigma_j \tag{20.14}$$

where $\hat{B}_j$ is to be chosen according to the Bogoliubov criterion. We anticipate that $\hat{B}_j$ will be independent of j ($\hat{B}_j = \hat{B}$), for all spins are equivalent. Thus

$$\mathscr{H}_0 = -(\hat{B} + B)\sum_j \sigma_j = -B^*\sum_j \sigma_j \tag{20.15}$$

where we define
$$B^* \equiv \hat{B} + B \tag{20.16}$$

Accordingly the "unperturbed" Helmholtz potential is

$$F_0 = -k_BT \ln \operatorname{tr} e^{-\beta\mathscr{H}_0} = -\tilde{N}k_BT \ln\{e^{+\beta B^*} + e^{-\beta B^*}\} \tag{20.17}$$

where $\tilde{N}$ is the number of sites in the lattice. The Bogoliubov inequality assures us that $F \leq F_0 + \langle \mathscr{H} - \mathscr{H}_0 \rangle_0$, or

$$F \leq F_0 - \sum_{i,j} J_{ij}\langle \sigma_i\sigma_j \rangle_0 + \hat{B}\tilde{N}\langle \sigma \rangle_0 \tag{20.18}$$

and we procede to calculate $\langle \sigma \rangle_0$ and $\langle \sigma_i\sigma_j \rangle_0$. In the unperturbed system the average of products centered on different sites simply factors;

$$\langle \sigma_i\sigma_j \rangle_0 = \langle \sigma_i \rangle_0 \langle \sigma_j \rangle_0 = \langle \sigma \rangle_0^2 \tag{20.19}$$

so that

$$F \leq F_0 - \tilde{N} J z_{nn} \langle \sigma \rangle_0^2 + (B^* - B)\tilde{N}\langle \sigma \rangle_0 \tag{20.20}$$

where z_{nn} is the number of nearest neighbors of a site in the lattice ($z_{nn} = 6$ for a simple cubic lattice, 8 for a body-centered cubic lattice, etc). Furthermore

$$\langle \sigma \rangle_0 = \frac{e^{\beta B^*} - e^{-\beta B^*}}{e^{\beta B^*} + e^{-\beta B^*}} = \tanh(\beta B^*) \tag{20.21}$$

We must minimize F with respect to $\hat{B}$. But from equations 20.20, 20.17 and 20.21 we observe that $\hat{B}$ appears in F only in the combination $\hat{B} + B \equiv B^*$. Hence we can minimize F with respect to B^*, giving the result that

$$B^* - B = \hat{B} = 2 z_{nn} J \langle \sigma \rangle_0 \tag{20.22}$$

This is a self-consistent condition, as $\langle \sigma \rangle_0$ is expressed in terms of B^* by equation 20.21.

Prior to analyzing this self-consistent solution for $\langle \sigma \rangle_0$, we observe its significance. If we were to seek $\langle \sigma \rangle$ in mean field theory we might proceed by differentiation (with respect to B) of the Helmholtz potential F (as calculated in mean field theory; equation 20.20). The applied field B appears explicitly in eq'n 20.20, *but it is also implicit in* $\langle \sigma \rangle_0$. Fortunately however, $\langle \sigma \rangle_0$ depends on B only in the combination $B + \hat{B} = B^*$ and we have imposed the condition that $\partial F / \partial B^* = 0$. Thus, in differentiation, only the *explicit* dependence of F on B need be considered. With this extremely convenient simplifying observation we immediately corroborate that differentiation of F (equation 20.20) with respect to B does give $\langle \sigma \rangle_0$. *The "spontaneous moment"* $\langle \sigma \rangle$ *in mean field theory is given properly by its zero-order approximation.*

Returning then to equation 20.21 for $\langle \sigma \rangle_0$ (and hence for $\langle \sigma \rangle$) the solution is best obtained graphically, as shown in Fig. 20.1. The abscissa of the graph is βB^*, or from equation 20.22

$$x \equiv \beta B^* = \beta(2 z_{nn} J \langle \sigma \rangle + B) \tag{20.23}$$

so that equation 20.21 can be written as

$$\langle \sigma \rangle = \frac{k_B T}{2 z_{nn} J} x - \frac{B}{2 z_{nn} J} = \tanh(x) \tag{20.24}$$

A plot of $\langle \sigma \rangle$ versus x from the first equality is a straight line of slope $k_B T / 2 z_{nn} J$ and of intercept $-B/2 z_{nn} J$. A plot of $\langle \sigma \rangle$ versus x from the second equality is the familiar $\tanh(x)$ curve shown in Fig. 20.1. The intersection of these two curves determines $\langle \sigma \rangle$.

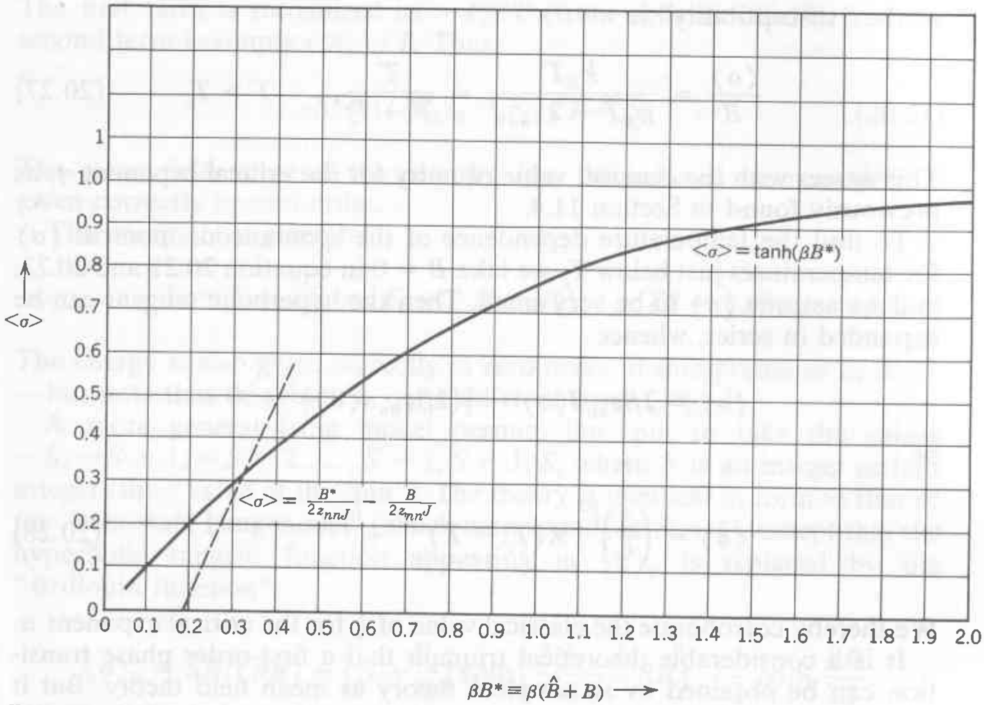


FIGURE 20.1

The qualitative behavior of $\langle \sigma(T, B)\rangle$ is evident. For $B = 0$, the straight line passes through the origin, with a slope $k_B T/2z_{nn}J$. The curve of $\tanh(x)$ has an initial slope of unity. Hence, if $k_B T/2z_{nn}J > 0$ the straight line and the $\tanh(x)$ curve have only the trivial intersection at $\langle\sigma\rangle = 0$. However, if $k_B T/2z_{nn}J < 1$ there is an intersection at a positive value of $\langle\sigma\rangle$ and another at a negative value of $\langle\sigma\rangle$, as well as the persistent intersection at $\langle\sigma\rangle = 0$. The existence of three formal solutions for $\langle\sigma\rangle$ is precisely the result we found in the thermodynamic analysis of first-order phase transitions in Chapter 9. A stability analysis there revealed the intermediate value $\langle\sigma\rangle = 0$ to be intrinsically unstable. The positive and negative values of $\langle\sigma\rangle$ are equally stable, and the choice of one or the other is an "accidental" event. We thus conclude that the system exhibits a first-order phase transition at low temperatures, and that the phase transition ceases to exist above the "Curie" temperature T_c given by

$$k_B T_c = 2z_{nn}J \tag{20.25}$$

We can also find the "susceptibility" for temperatures above T_c. For small arguments $\tanh y \simeq y$, so that equation 20.24 becomes, for $T > T_c$,

$$\langle\sigma\rangle \simeq \beta(2z_{nn}J\langle\sigma\rangle + B), \qquad T > T_c \tag{20.26}$$

or the "susceptibility" is

$$\frac{\langle\sigma\rangle}{B} = \frac{k_B T}{k_B T - 2z_{nn}J} = \frac{T}{T - T_c}, \qquad T > T_c \tag{20.27}$$

This agrees with the classical value of unity for the critical exponent γ, as previously found in Section 11.4.

To find the temperature dependence of the spontaneous moment $\langle\sigma\rangle$ for temperatures just below T_c we take $B = 0$ in equation 20.21 and 20.22, and we assume $\langle\sigma\rangle$ to be very small. Then the hyperbolic tangent can be expanded in series, whence

$$\langle\sigma\rangle = 2\beta z_{nn}J\langle\sigma\rangle - \tfrac{1}{3}(2\beta z_{nn}J\langle\sigma\rangle)^3 + \cdots$$

or

$$\langle\sigma\rangle = \left(\frac{3}{T_c}\right)^{1/2} \times (T_c - T)^{1/2} + \cdots \tag{20.28}$$

We thereby corroborate the classical value of $\frac{1}{2}$ for the critical exponent α.

It is a considerable theoretical triumph that a first-order phase transition can be obtained by so simple a theory as mean field theory. But it must be stressed that the theory is nevertheless rather primitive. In reality the Ising model does not have a phase transition in one dimension, though it does in both two and three dimensions. Mean field theory, in contrast, predicts a phase transition without any reference to the dimensionality of the crystalline array. And, of course, the subtle details of the critical transitions, as epitomized in the values of the critical exponents, are quite incorrect.

Finally, it is instructive to inquire as to the thermal properties of the system. In particular we seek the mean field value of the entropy $S = -(\partial F/\partial T)_V$. We exploit the stationarity of F with respect to B^* by rewriting equation 20.20, with B^* rewritten as $(k_B T\beta B^*)$

$$F = -\tilde{N}k_B T\ln\left[e^{\beta B^*} + e^{-\beta B^*}\right] - \tilde{N}Jz_{nn}\langle\sigma\rangle^2$$
$$+ \tilde{N}k_B T(\beta B^*)\langle\sigma\rangle - \tilde{N}B\langle\sigma\rangle \tag{20.29}$$

Then in differentiating F with respect to T we can treat βB^* as a constant

$$S = -\left(\frac{\partial F}{\partial T}\right)_{\beta B^*, \langle\sigma\rangle} = \tilde{N}k_B\ln\left[e^{\beta B^*} + e^{-\beta B^*}\right] - \tilde{N}k_B(\beta B^*)\langle\sigma\rangle \tag{20.30}$$

The first term is recognized as $-F_0/T$ (from equation 20.17), and the second term is simply $\langle \mathscr{H}_0 \rangle /T$. Thus

$$S = (\langle \mathscr{H}_0 \rangle_0 - F_0)/T = S_0 \tag{20.31}$$

The mean field value of the entropy, like the induced moment $\langle \sigma \rangle$, is given correctly in zero order.

The energy U is given by

$$U = F + TS = (F_0 + \langle \mathscr{H} - \mathscr{H}_0 \rangle_0) + TS = \langle \mathscr{H} \rangle_0 \tag{20.32}$$

The energy is also given correctly in zero order, if interpreted as in 20.32 —but note that this result is quite different from $\langle \mathscr{H}_0 \rangle_0$!

A more general Ising model permits the spin to take the values $-S, -S+1, -S+2, \ldots, S-2, S-1, S$, where S is an integer or half integer (the "value of the spin"). The theory is identical in form to that of the "two-state Ising model" (which corresponds to $S = \frac{1}{2}$), except that the hyperbolic tangent function appearing in $\langle \sigma \rangle_0$ is replaced by the "Brillouin function":

$$\langle \sigma \rangle_0 = SB_S(\beta B) = \left(S + \frac{1}{2}\right) \coth\left(\frac{2S+1}{2S}\beta B\right) - \frac{1}{2} \coth \frac{\beta B}{2S} \tag{20.33}$$

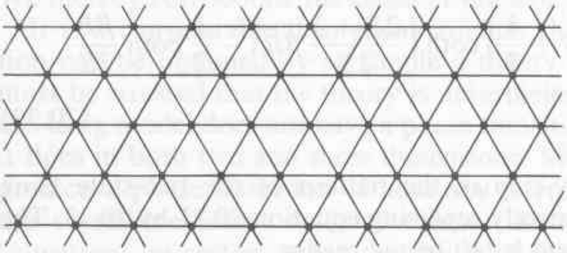
The analysis follows step-by-step in the pattern of the two-state Ising model considered above — merely replacing equation 20.21 by 20.33. The corroboration of this statement is left to the reader.

In a further generalization, the Heisenberg model of ferromagnetism permits the spins to be quantum mechanical entities, and it associates the external "field" B with an applied magnetic field B_e. Within the mean field theory, however, only the component of a spin along the external field axis is relevant, and the quantum mechanical Heisenberg model reduces directly to the classical Ising model described above. Again the reader is urged to corroborate these conclusions, and he or she is referred to any introductory text on the theory of solids for a more complete discussion of the details of the calculation and of the consequences of the conclusions.

The origin of the name "mean field theory" lies in the heuristic reasoning that led us to a choice of a soluble model Hamiltonian in the Ising (or Heisenberg) problem above. Although each spin interacts with other spins, the mean field approach effectively replaces the bi-linear spin interaction $\sigma_i \sigma_j$ by a linear term $B_j \sigma_j$. The quantity B_j plays the role of an effective magnetic field acting on σ_j, and the optimum choice of B_j is $\langle \sigma \rangle$. Equivalently, the product $\sigma_i \sigma_j$ is "linearized," replacing one factor by its average value. A variety of recipes to accomplish this in a consistent manner exist. However we caution against such recipes, as they generally substitute heuristic appeal for the well-ordered rigor of the Bogoliubov inequality, and they provide no sequence of successive improvements. More immediately, the stationarity of F to variations in B^* greatly simplifies differentiation of F (required to evaluate thermodynamic quantities; recall equation 20.30), and the analogue of this stationarity has no basis in heuristic formulations. But most important, there are applications of the "mean field" formalism (as based on the Bogoliubov inequality) in which products of operators are *not* simply "linearized." For these the very name "mean field" is a misnomer. A simple and instructive case of this type is given in the following Example.

Example

N Ising spins, each capable of taking *three* values ($\sigma = -1, 0, +1$) form a planar triangular array, as shown. Note that there are $2N$ triangles for N spins, and that each spin is shared by six triangles. We assume N to be sufficiently large that edge effects can be ignored.



The energy associated with each triangle (a three-body interaction) is

$$\begin{gathered} -\varepsilon \text{ if two spins are "up"} \\ -2\varepsilon \text{ if three spins are "up"} \\ 0 \text{ otherwise} \end{gathered}$$

Calculate (approximately) the number of spins in each spin state if the system is in equilibrium at temperature T.

Solution

The problem differs from the Ising and Heisenberg prototypes in two respects; we are not given an analytic representation of the Hamiltonian (though we could devise one with moderate effort), and a "mean field" type of model Hamiltonian (of the form $B\Sigma_j\sigma_j$) would not be reasonable. This latter observation follows from the stated condition that the energies of the various possible configurations depend only on the populations of the "up" states, and that there is no distinction in energy between the $\sigma = 0$ and the $\sigma = -1$ states. The soluble model Hamiltonian should certainly preserve this symmetry, which a mean-field type Hamiltonian does not do. Accordingly we take as the soluble model Hamiltonian one in which the energy $-\hat{\varepsilon}$ is associated with each "up" spin in the lattice (the $\sigma = 0$ and -1 states each having zero energy). The energy $\hat{\varepsilon}$ will be the variational parameter of the problem.

The "unperturbed" value of the Helmholtz potential is determined by

$$e^{-\beta F_0} = \left(e^{\beta\hat{\varepsilon}} + 2\right)^N$$

and the probability that a spin is up, to zero order, is

$$f_{0\uparrow} = \frac{e^{\beta\hat{\varepsilon}}}{\left(e^{\beta\hat{\varepsilon}} + 2\right)} = \left(1 + 2e^{-\beta\hat{\varepsilon}}\right)^{-1}$$

whereas $$f_{0\downarrow} = f_{0\rightarrow} = \frac{(1 - f_{0\uparrow})}{2}$$

Within each triangle the probability of having all three spins up is $f_{0\uparrow}^3$, and the probability of having two spins up is $3f_{0\uparrow}^2(1 - f_{0\uparrow})$. We can now calculate $\langle \mathscr{H} \rangle_0$ and $\langle \mathscr{H}_0 \rangle_0$ directly:

$$\langle \mathscr{H}_0 \rangle_0 = -N\hat{\varepsilon} f_0$$

whereas $$\langle \mathscr{H} \rangle_0 = 2N\varepsilon\left\{-2f_{0\uparrow}^3 - 3f_{0\uparrow}^2(1 - f_{0\uparrow})\right\} = 2N\varepsilon\left\{f_{0\uparrow}^3 - 3f_{0\uparrow}^2\right\}$$

The variational condition then is

$$F \leq -Nk_BT\ln\left(e^{\beta\hat{\varepsilon}} + 2\right) + 2N\left\{\varepsilon f_{0\uparrow}^3 - 3\varepsilon f_{0\uparrow}^2\right\} + N\hat{\varepsilon} f_{0\uparrow}$$

It is convenient to express the argument of the logarithm in terms of f_0;

$$F \leq -Nk_BT\ln\left[\frac{2}{(1 - f_{0\uparrow})}\right] + 2N\left[\varepsilon f_{0\uparrow}^3 - 3f_{0\uparrow}^2\right] + N\hat{\varepsilon} f_{0\uparrow}$$

The variational parameter $\hat{\varepsilon}$ appears explicitly only in the last term, but it is also implicit in $f_{0\uparrow}$. It is somewhat more convenient to minimize F with respect to $f_{0\uparrow}$ (inverting the functional relationship $f_{0\uparrow}(\hat{\varepsilon})$ to consider $\hat{\varepsilon}$ as a function of $f_{0\uparrow}$)

$$0 = \frac{dF}{df_{0\uparrow}} = \frac{-Nk_BT}{(1 - f_{0\uparrow})} + 6N\varepsilon f_{0\uparrow}^2 - 12N\varepsilon f_{0\uparrow} + N\hat{\varepsilon} + Nf_{0\uparrow}\left(\frac{d\hat{\varepsilon}}{df_{0\uparrow}}\right)$$

The last term is easily evaluated to be $Nk_BT\left[f_{0\uparrow}^{-1} + (1 - f_{0\uparrow})^{-1}\right]$, so that the variational condition becomes

$$6\beta\varepsilon f_{0\uparrow}^3 - 12\beta\varepsilon f_{0\uparrow}^2 + f_{0\uparrow}\ln\left[\frac{2f_{0\uparrow}}{(1 - f_{0\uparrow})}\right] + 1 = 0$$

This equation must be solved numerically or graphically. Given the solution for $f_{0\uparrow}$ (as a function of the temperature) the various physical properties of the system can be calculated in a straightforward manner.

PROBLEMS

20.2-1. Formulate the exact solution of the two-particle Ising model with an external "field" (assume that each particle can take only two states; $\sigma = -1$ or $+1$). Find both the "magnetization" and the energy, and show that there is no phase transition in zero external field. Solve the problem by mean field theory, and show that a transition to a spontaneous magnetization in zero external field is predicted to occur at a non-zero temperature T_c. Show that below T_c the spontaneous moment varies as $(T - T_c)^{\beta}$ and find T_c and the critical exponent β (recall Chapter 11).

20.2-2. Formulate mean field theory for the three state Ising model (in which the variables σ_j in equation 20.13 can take the three values $-1, 0, +1$). Find the "Curie" temperature T_c (as in equation 20.25).

20.2-3. For the Heisenberg ferromagnetic model the Hamiltonian is

$$\mathscr{H} = -\sum_{i,j} J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j - (\mu_B B_e)\sum_j S_{jz}$$

where μ_B is the Bohr magneton and B_e is the magnitude of the external field, which is assumed to be directed along the z axis. The z-components of S_j are quantized, taking the permitted values $S_{jz} = -S, -S+1, \ldots, S-1, S$. Show that for $S = \frac{1}{2}$ the mean field theory is identical to the mean field theory for the two-state Ising model if $2S$ is associated with σ and if a suitable change of scale is made in the exchange interaction parameter J_{ij}. Are corresponding changes of scale required for the $S = 1$ case (recall Problem 20.2-1), and if so, what is the transformation?

20.2-4. A metallic surface is covered by a monomolecular layer of $\tilde{N}$ organic molecules in a square array. Each adsorbed molecule can exist in two steric configurations, designated as oblate and prolate. Both configurations have the same energy. However two nearest neighbor molecules mechanically interfere if, and only if, both are oblate. The energy associated with such an oblate–oblate interference is ε (a positive quantity). Calculate a reasonable estimate of the number of molecules in each configuration at temperature T.

20.2-5. Solve the preceding problem if the molecules can exist in three steric configurations, designated as oblate, spherical and prolate. Again all three configurations have the same energy. And again two nearest-neighbor molecules interfere if, and only if, both are oblate; the energy of interaction is ε. Calculate (approximately) the number of molecules in each configuration at temperature T.

Answer:

$\tilde{N}/10$ at $k_B T/\varepsilon \simeq 0.266$; $\tilde{N}/5$ at $k_B T/\varepsilon \simeq 1.15$

$\tilde{N}/4$ at $k_B T/\varepsilon \simeq 2.47$; $3\tilde{N}/10$ at $k_B T/\varepsilon \simeq 7.78$

$\tilde{N}/3$ at $k_B T \rightarrow \infty$

20.2-6. In the classical Heisenberg model each spin can take any orientation in space (recall that the classical partition function of a single spin in an external field B is $z_{\text{classical}} = \int e^{-\beta BS\cos\theta}\sin\theta\, d\theta\, d\phi$. Show that, in mean field theory,

$$\langle S_z \rangle = S\coth\left[\beta(\hat{B}+B)S\right] - \frac{S}{\left[\beta(\hat{B}+B)S\right]}$$

20.2-7. $2\tilde{N}$ two-valued Ising spins are arranged sequentially on a circle, so that the last spin is a neighbor of the first. The Hamiltonian is

$$\mathscr{H} = 2\sum_{j=1}^{2\tilde{N}} J_j \sigma_j \sigma_{j+1} - B\sum_j \sigma_j$$

where $J_j = J_e$ if j is even and $J_j = J_0$ if j is odd. Assume $J_0 > J_e$.

There are two options for carrying out a mean field theory for this system. The first option is to note that all spins are equivalent. Hence one can choose an unperturbed system of $2\tilde{N}$ single spins, each acted on by an effective field (to be evaluated variationally). The second option is to recognize that we can choose a pair of spins coupled by J_0 (the larger exchange interaction). Each such pair is coupled to two other pairs by the weaker exchange interactions J_e. The unperturbed system consists of $\tilde{N}$ such pairs.

Carry out each of the mean field theories described above. Discuss the relative merits of these two procedures.

20.2-8. Consider a sequence of $2\tilde{N}$ alternating A sites and B sites, the system being arranged in a circle so that the $(2\tilde{N})^{\text{th}}$ site is the nearest neighbor of the first site. Even numbered sites are occupied by two-valued Ising spins, with $\sigma_j = \pm 1$. Odd numbered sites are occupied by three-valued Ising spins, with $\sigma_j = -1, 0, +1$. The Hamiltonian is

$$\mathscr{H} = -2J\sum_j \sigma_j \sigma_{j+1} - B\sum_j \sigma_j$$

a) Formulate a mean field theory by choosing as a soluble model system a collection of independent A sites and a collection of independent B sites, each acted upon by a different mean field.

b) Formulate a mean field theory by choosing as a soluble model system a collection of $\tilde{N}$ independent A–B pairs, with the Hamiltonian of each pair being

$$\mathscr{H}_{\text{pair}} = -2J\sigma_{\text{odd}}\sigma_{\text{even}} + B_{\text{odd}}\sigma_{\text{odd}} + B_{\text{even}}\sigma_{\text{even}}$$

c) Are these two procedures identical? If so, why? If not, which procedure would you judge to be superior, and why?

20-3 MEAN FIELD IN GENERALIZED REPRESENTATION: THE BINARY ALLOY

Mean field theory is slightly more general than it might at first appear from the preceding discussion. The larger context is clarified by a particular example. We consider a binary alloy (recall the discussion of Section 11.3) in which each site of a crystalline array can be occupied by either an A atom or a B atom. The system is in equilibrium with a thermal and particle reservoir, of temperature T and of chemical potentials (i.e., partial molar Gibbs potentials) μ_A and μ_B. The energy of an A atom in the crystal is ε_A, and that of a B atom is ε_B. In addition neighboring A atoms have an interaction energy ε_{AA}, neighboring B atoms have an interaction energy ε_{BB}, and neighboring A–B pairs have an interaction energy ε_{AB}.

We are interested not only in the number of A atoms in the crystal, but in the extent to which the A atoms either segregate separately from the B atoms or intermix regularly in an alternating $ABAB$ pattern. That is, we seek to find the average numbers $\tilde{N}_A$ and $\tilde{N}_B$ of each type of atom, and the average numbers $\tilde{N}_{AA}$, $\tilde{N}_{AB}$, and $\tilde{N}_{BB}$ of each type of nearest neighbor pair. These quantities are to be calculated as a function of T, μ_A and μ_B.

The various numbers $\tilde{N}_A, \tilde{N}_{AB}, \ldots$ are not all independent, for

$$\tilde{N}_A + \tilde{N}_B = \tilde{N} \tag{20.34}$$

and by counting the number of "bonds" emanating from A atoms

$$2\tilde{N}_{AA} + \tilde{N}_{AB} = z_{nn}\tilde{N}_A \tag{20.35}$$

Similarly

$$2\tilde{N}_{BB} + \tilde{N}_{AB} = z_{nn}\tilde{N}_B \tag{20.36}$$

where we recall that z_{nn} is the number of nearest neighbors of a single site. Consequently all five numbers are determined by two, which are chosen conveniently to be $\tilde{N}_A$ and $\tilde{N}_{AA}$.

The energy of the crystal clearly is

$$E = \tilde{N}_A\varepsilon_A + \tilde{N}_B\varepsilon_B + \tilde{N}_{AA}\varepsilon_{AA} + \tilde{N}_{AB}\varepsilon_{AB} + \tilde{N}_{BB}\varepsilon_{BB} \tag{20.37}$$

If we associate with each site an Ising spin such that the spin is "up" ($\sigma = +1$) if the site is occupied by an A atom, and the spin is "down" ($\sigma = -1$) if the spin is occupied by a B atom, then

$$\mathscr{H} = C - \sum_i \sum_j J_{ij}\sigma_i\sigma_j - \hat{B}\sum_i \sigma_i \tag{20.38}$$

where

$$J = \tfrac{1}{4}\varepsilon_{AB} - \tfrac{1}{8}\varepsilon_{AA} - \tfrac{1}{8}\varepsilon_{BB} \tag{20.39}$$

$$\hat{B} = \tfrac{1}{2}(\varepsilon_{BB} - \varepsilon_{AA}) + \tfrac{1}{4}z_{nn}(\varepsilon_{AA} + \varepsilon_{BB}) \tag{20.40}$$

$$C = \tfrac{1}{8}\tilde{N}(4\varepsilon_A + 4\varepsilon_B + z_{nn}\varepsilon_{AA} + 2z_{nn}\varepsilon_{AB} + z_{nn}\varepsilon_{BB}) \tag{20.41}$$

These values of J, $\hat{B}$, and C can be obtained in a variety of ways. One simple approach is to compare the values of E (equation 20.37) and of $\mathscr{H}$ (equation 20.38) in the three configurations in which (a) all sites are occupied by A atoms, (b) all sites are occupied by B atoms, and (c) equal numbers of A and B atoms are randomly distributed.

Except for the inconsequential constant C, the Hamiltonian is now that of the Ising model. However, the physical problem is quite different. We must recall that the system is in contact with particle reservoirs of chemical potentials μ_A and μ_B, as well as with a thermal reservoir of temperature T. The problem is best solved in a grand canonical formalism.

The essential procedure in the grand canonical formalism is the calculation of the grand canonical potential $\Psi(T, \mu_A, \mu_B)$ by the algorithm[3]

$$e^{-\beta\Psi} = \operatorname{tr} e^{-\beta(\mathscr{H} - \tilde{\mu}_A \tilde{N}_A - \tilde{\mu}_B \tilde{N}_B)} \tag{20.42}$$

This is isomorphic with the canonical formalism (on which the mean field theory of Section 20.2 was based) if we simply replace the Helmholtz potential F by the grand canonical potential Ψ, and replace the Hamiltonian $\mathscr{H}$ by the "grand canonical Hamiltonian" $\mathscr{H} - \tilde{\mu}_A \tilde{N}_A - \tilde{\mu}_B \tilde{N}_B$.

In the present context we augment the Hamiltonian 20.38 by terms of the form $-\frac{1}{2}[(\tilde{\mu}_A + \tilde{\mu}_B) + (\tilde{\mu}_A - \tilde{\mu}_B)\Sigma_i \sigma_i]$. The grand canonical Hamiltonian is then

$$\mathscr{H}' = C' - \sum_i \sum_j J_{ij} \sigma_i \sigma_j - \hat{B}' \sum_i \sigma_i \tag{20.43}$$

where

$$C' = C - \tfrac{1}{2}\tilde{N}(\tilde{\mu}_A + \tilde{\mu}_B) \tag{20.44}$$

and

$$\hat{B}' = \hat{B} - \tfrac{1}{2}(\tilde{\mu}_A - \tilde{\mu}_B) \tag{20.45}$$

The analysis of the Ising model then applies directly to the binary alloy problem (with the Helmholtz potential being reinterpreted as the grand canonical potential). Again mean field theory predicts an order–disorder phase transition. Again that prediction agrees with more rigorous theory in two and three dimensions, whereas a one-dimensional binary crystal should not have an order–disorder phase transition. And again the critical exponents are incorrectly predicted.

More significantly, the general approach of mean field theory is applicable to systems in generalized ensembles, requiring only the reinterpretation of the thermodynamic potential to be calculated, and of the effective "Hamiltonian" on which the calculation is to be based.

---

[3] $\tilde{\mu}_A$ ($\equiv \mu_A$/Avogadro's number) is the chemical potential *per particle*.