

PHASE TRANSITION IN A ONE-DIMENSIONAL SYSTEM, II*

BY TERRELL L. HILL† AND GEORGE M. WHITE

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF OREGON, EUGENE

Communicated May 22, 1967

In the previous paper¹ (Part I), we examined a simple model which leads to a first-order phase transition in a one-dimensional system. The present work is an extension of that paper. We use the same notation and fundamental equations; these will not be repeated here.

In Part I, the intermolecular pair potential for adsorbed molecules, $w_2(r)$, was a step function. Here we take $w_2(r)$ to be a smooth function of r . We find, in the examples considered, a phase transition whether $w_2(r)$ is attractive or repulsive. The critical behavior, unlike that found in Part I, is "normal."

As in Part I, uniform lattice spacing is required to produce a phase transition. Nonuniform spacing cannot give a transition.

Uniform Lattice Spacing (Attraction).—As our first example, let us use the Lennard-Jones functions

$$\frac{w_1(x)}{kT} = -\frac{2\epsilon}{kT} \left(\frac{1}{x}\right)^6 + \frac{\epsilon}{kT} \left(\frac{1}{x}\right)^{12}, \quad (1)$$

$$\frac{w_2(x)}{kT} = -\frac{2\epsilon}{kT} \left(\frac{1.15}{x}\right)^6 + \frac{\epsilon}{kT} \left(\frac{1.15}{x}\right)^{12}, \quad (2)$$

$$x = r/r_1^*, \quad r_2^* = 1.15r_1^*. \quad (3)$$

This is, of course, a quite arbitrary choice. The two potential functions have the same depth; the adsorbed molecules are 15 per cent too large for the lattice. Consequently the lattice will start with $r = r_1^*$, $x = 1$, when $\lambda = q_2\lambda_2 = 0$ and will expand as λ increases (T constant). Below the critical temperature there will be a sudden jump in the value of x and in the value of $\theta = \bar{N}_2/N_1$ at a certain λ , $\lambda = \lambda_c$.

Because of the step function used for $w_2(r)$ in Part I, the exact form of $w_1(r)$ did not have to be specified. But here it is necessary. Incidentally, in a polymer system, $w_1(r)$ could originate as a configurational entropy term, rather than as potential energy. In general, $w_1(r)$ would be a free energy.

The variable x is a parameter of the system. For a given value of x [see equation (I-2)],

$$\gamma_m(x)^{N_1} = e^{-N_1\mu_1(x)/kT} = \sum_{N_2} e^{N_2\mu_2/kT} Q(N_1, N_2, T, x). \quad (4)$$

Strictly speaking, to relate this equation to thermodynamics, we should integrate over x . But since the system is macroscopic, we can just as well (and more simply) use that value of x , x^* , which minimizes $\mu_1(x)$ or maximizes $\gamma_m(x)$, and omit the integration.

Similarly, if we work with

$$e^{-A(x)/kT} = Q(N_1, N_2, T, x), \quad (5)$$

we can again omit an integration over x and instead minimize A with respect to x

(or maximize Q). Because of the insensitivity of thermodynamic properties of macroscopic systems to the choice of partition function, the same x^* will of course be involved in equations (4) and (5).

For a particular value of x , we have simply an ordinary one-dimensional Ising problem² (with no phase transition). We use the matrix method, and equation (4). A site (a "unit") can be empty [matrix entry $q_1z(x)$] or occupied [matrix entry $q_1z(x)\lambda$], where $z(x) = e^{-w_1(x)/kT}$. If a site and the site to its right are both occupied, there is a further factor $u(x) = e^{-w_2(x)/kT}$ to be entered in the matrix. Hence the secular equation is

$$\begin{vmatrix} q_1z(x) - \gamma & q_1z(x) \\ q_1z(x)\lambda & q_1z(x)u(x)\lambda - \gamma \end{vmatrix} = 0. \quad (6)$$

This gives

$$\gamma_m(x) = \frac{q_1z(x)}{2} \langle 1 + \lambda u(x) + \{ [1 - \lambda u(x)]^2 + 4\lambda \}^{1/2} \rangle. \quad (7)$$

This is essentially equation (I-5).

Figure 1 illustrates equations (1) to (3), and (7). We plot $\gamma_m(x)/q_1$ as a function

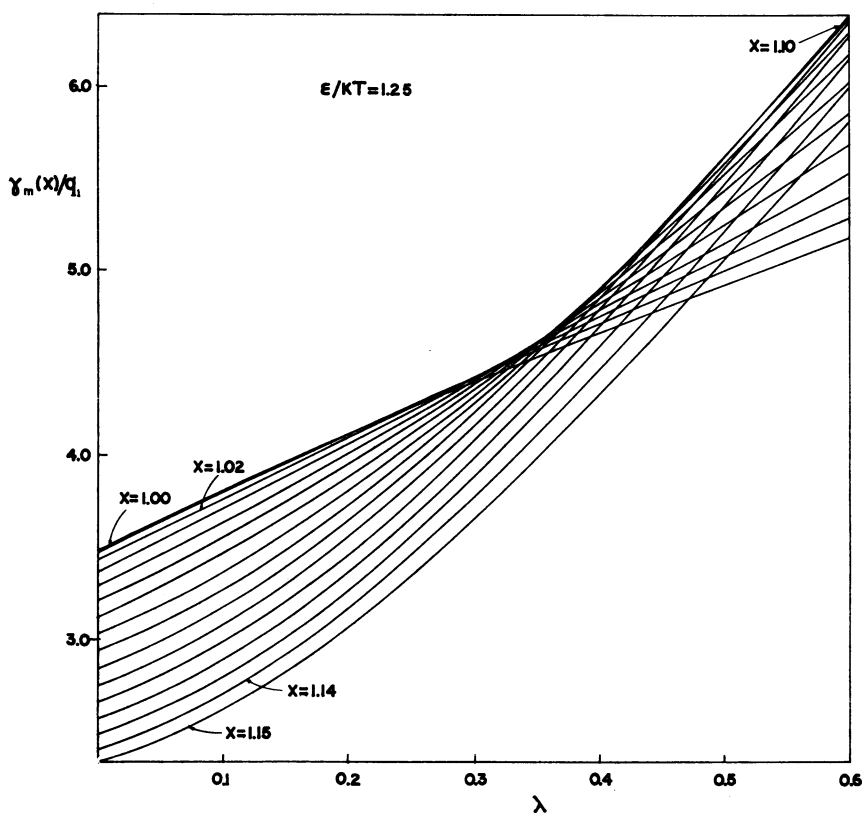


FIG. 1.—The envelope is a plot of $e^{-\mu_1/kT}/q_1$ against $q_2\lambda_2$ at a temperature above the critical temperature.

of λ for $\epsilon/kT = 1.25$, and for a number of different values of x . The envelope is the thermodynamic value of $e^{-\mu/kT}/q_1$. That is, for each λ , we select that value of x , x^* , which maximizes $\gamma_m(x)/q_1$. The value of x^* changes smoothly as λ increases. There is no phase transition (this temperature is above the critical temperature). When λ is small, $x^* = 1$, as already mentioned above. When λ is very large, all sites will be occupied and the system will choose that value of x which minimizes the total potential energy per site, $w_1(x) + w_2(x)$. From equations (1) and (2), we find $x^* = 1.115$ for $\lambda \rightarrow \infty$, irrespective of the value of ϵ/kT . We note also that when $\lambda \rightarrow \infty$, $\gamma_m(x) \rightarrow q_1 z(x) u(x) \lambda$, which of course leads to the same result.

Figure 2 gives a similar plot for the case $\epsilon/kT = 3.00$. There is a phase transition at $\lambda_t = 0.118$, where a sudden jump in x^* occurs, from a value near 1.00 to one near 1.11.

Figure 3, for $\epsilon/kT = 1.50$, is very close to the critical temperature (note the number of lines intersecting practically at the transition point). The critical value of ϵ/kT appears to be slightly less than 1.50.

There is a similar clustering of intersecting lines "submerged" in those figures with $T < T_c$ (see, for example, Figs. 2 and 7). In such a case, if we imagine con-

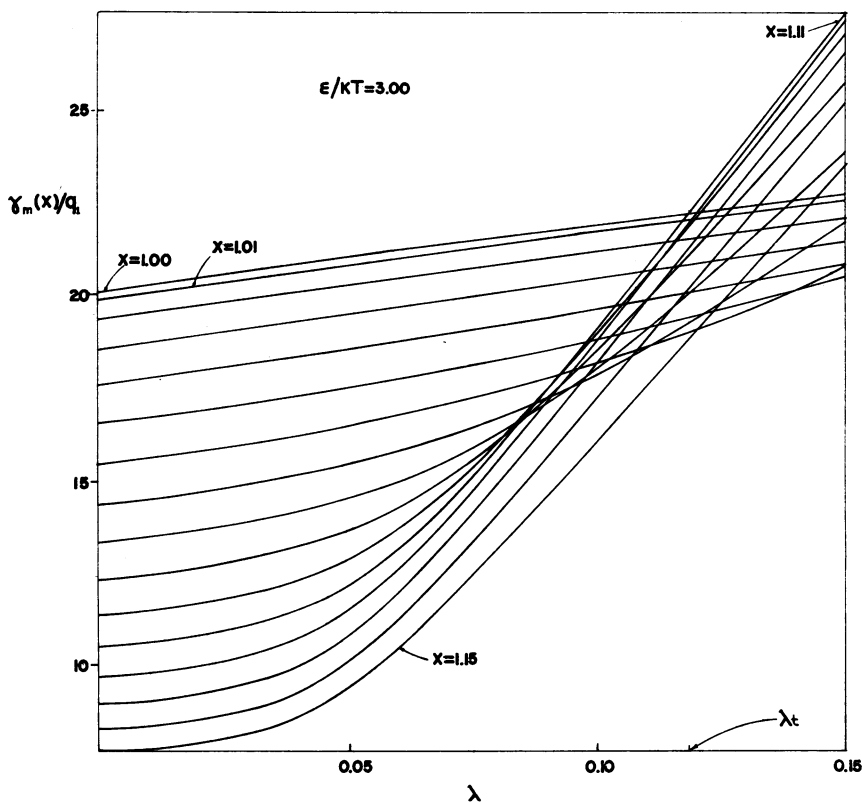


FIG. 2.—The envelope is a plot of $e^{-\mu/kT}/q_1$ against $q_2 \lambda_2$ at a temperature below the critical temperature. The phase transition is at $\lambda = \lambda_t$.

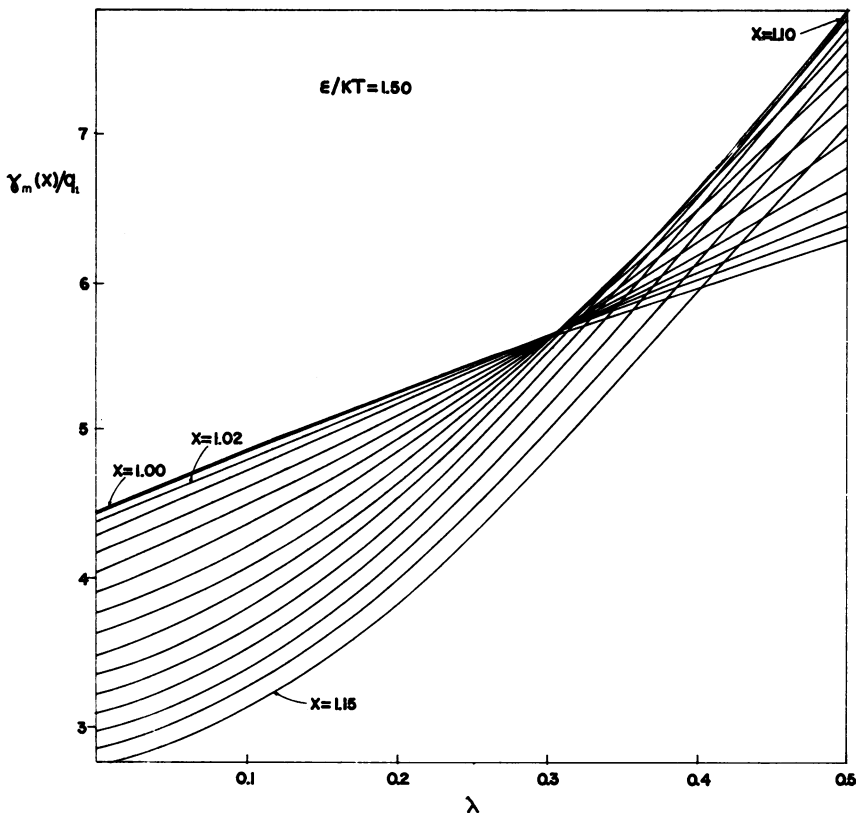


FIG. 3.—The envelope is a plot of $e^{-\mu_1/kT}/q_1$ against $q_2\lambda_2$ very near the critical temperature.

straining the system to values of x larger than an appropriately chosen value (so that the cluster of lines is brought to the “surface”), then T becomes a new “critical temperature.”

The adsorption isotherm, θ as a function of λ , can be obtained from the slope of the envelope in Figures 1 to 3. This follows because [see equation (I-4)]

$$\theta = \left[\frac{\partial \ln \gamma_m(x^*)}{\partial \ln \lambda} \right]_T \tag{8}$$

For example, the isotherm $ABCD$ in Figure 4 has been calculated from Figure 2 ($\epsilon/kT = 3.00$). The discontinuity in the slope of the envelope in Figure 2 leads to a discontinuity in θ in Figure 4.

Alternatively, thermodynamic properties may be calculated from equation (5) (canonical ensemble). As already mentioned, equation (7) is essentially the standard Ising result (for a given x). The corresponding expression² for $A(x)$ is

$$\begin{aligned} \frac{A(x)}{N_1kT} = & - \ln q_1 - \theta \ln q_2 + \theta \ln \frac{\beta(x) - 1 + 2\theta}{\beta(x) + 1 - 2\theta} + \ln \frac{\beta(x) + 1 - 2\theta}{\beta(x) + 1} \\ & + \frac{w_1(x)}{kT} + \frac{\theta w_2(x)}{kT}, \tag{9} \end{aligned}$$

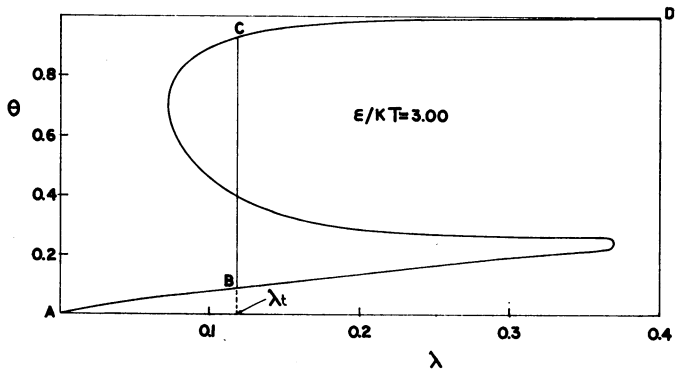


FIG. 4.—Adsorption isotherm (ABCD), θ against λ , for $\epsilon/kT = 3.00$ (as in Fig. 2). The phase transition is at $\lambda = \lambda_t$. The loop follows from equation (11) and Fig. 6.

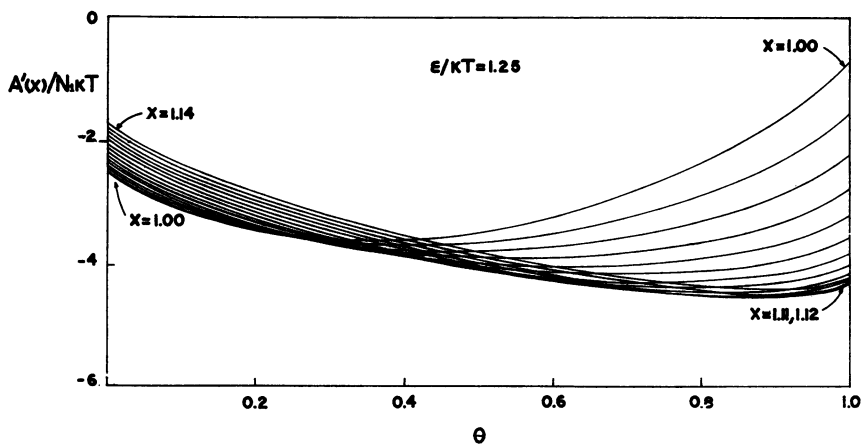


FIG. 5.—The envelope is a plot of the free energy, A'/N_1kT against θ for $\epsilon/kT = 1.25$ (as in Fig. 1). There is no phase transition.

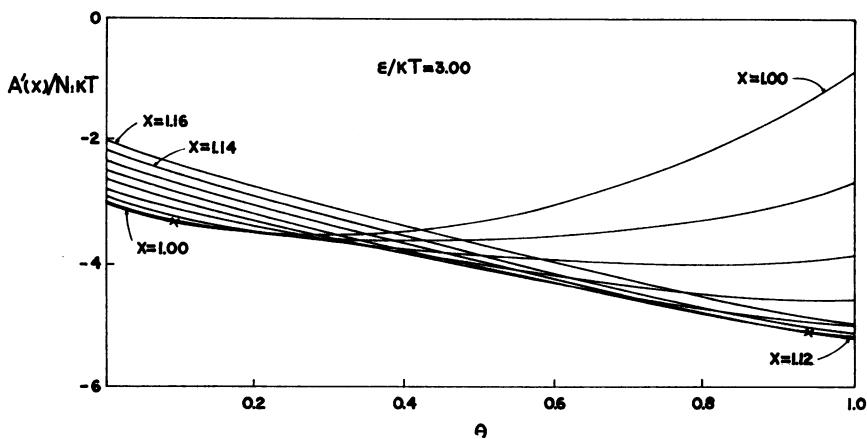


FIG. 6.—The envelope is a plot of the free energy, A'/kT against θ for $\epsilon/kT = 3.00$ (as in Fig. 2). The two crosses on the envelope mark the two phases in the phase transition.

where

$$\beta(x)^2 = 1 - 4\theta(1 - \theta)[1 - u(x)].$$

As an illustration, we plot, in Figure 5, $A'(x)/N_1kT$ against θ , for $\epsilon/kT = 1.25$ and various values of x , where

$$\frac{A'(x)}{N_1kT} = \frac{A(x)}{N_1kT} + \ln q_1 + \theta \ln q_2. \quad (10)$$

This is the same case as in Figure 1. Here, the lower envelope, minimizing $A(x)$ for each θ , gives the thermodynamic free energy.

Figure 6 shows $A'(x)/N_1kT$ versus θ for $\epsilon/kT = 3.00$. The envelope exhibits the phase transition found in Figure 2: a straight line can be drawn between the two arrows, tangent to the envelope at both points. To obtain the adsorption isotherm here, we use

$$\left[\frac{\partial A'(x^*)/N_1kT}{\partial \theta} \right]_T = \ln \lambda. \quad (11)$$

From this equation we find that the slope of the envelope in Figure 6 leads to the loop in Figure 4. The vertical jump is not found because this is a closed system³: for a value of θ between the arrows in Figure 6, the system is constrained to use a single x^* (not corresponding to either stable phase). In the open system of Figure 2, a value of θ in the same range can be achieved by the system spending part of its time in each of the two stable phases (at λ_i).

The location of the vertical jump in Figure 4 is consistent with the shape of the loop, incidentally. This has been verified by use of the appropriate equal area theorem (θ versus $\ln \lambda$).

Uniform Lattice Spacing (Repulsion).—As a second example, let us use $w_1(x)/kT$ in equation (1) again, but for $w_2(x)$ we take the repulsive interaction,

$$\frac{w_2(x)}{kT} = \frac{\epsilon}{kT} \left(\frac{1}{x} \right)^{12}. \quad (12)$$

Thus the lattice will have $x^* = 1$ at $\lambda = 0$ but will expand as λ increases. In fact, in the limit $\lambda \rightarrow \infty$, we find, as above, that $x^* = 1.122$.

Critical behavior is "normal." The critical value of ϵ/kT appears to be a little above 4.00. Figure 7 shows $\gamma_m(x)/q_1$ as a function of λ for $\epsilon/kT = 5.00$. Figure 8 shows $A'(x)/N_1kT$ versus θ for $\epsilon/kT = 12.00$. For large ϵ/kT , the densities of the two phases approach $\theta = 0.50$ and $\theta = 1.00$, as expected.

Nonuniform Lattice Spacing.—Consider the model discussed so far in this paper, but with the modification that each lattice spacing between two sites can have any value of x , irrespective of other lattice spacings. When both sites are occupied, the potential energy of the pair of sites is $w_1(x) + w_2(x)$. When both sites are not occupied, the potential energy is $w_1(x)$. This is still, basically, a simple Ising problem. We use the matrix method. A "unit" is, say, a site and the spacing to its right. An empty site has a matrix entry q_1 ; an occupied site has $q_1\lambda$. The nearest-neighbor interaction entry, when both sites are occupied, we write as $\int e^{-[w_1(x) + w_2(x)]/kT} dx$. Otherwise it is $\int e^{-w_1(x)/kT} dx$.

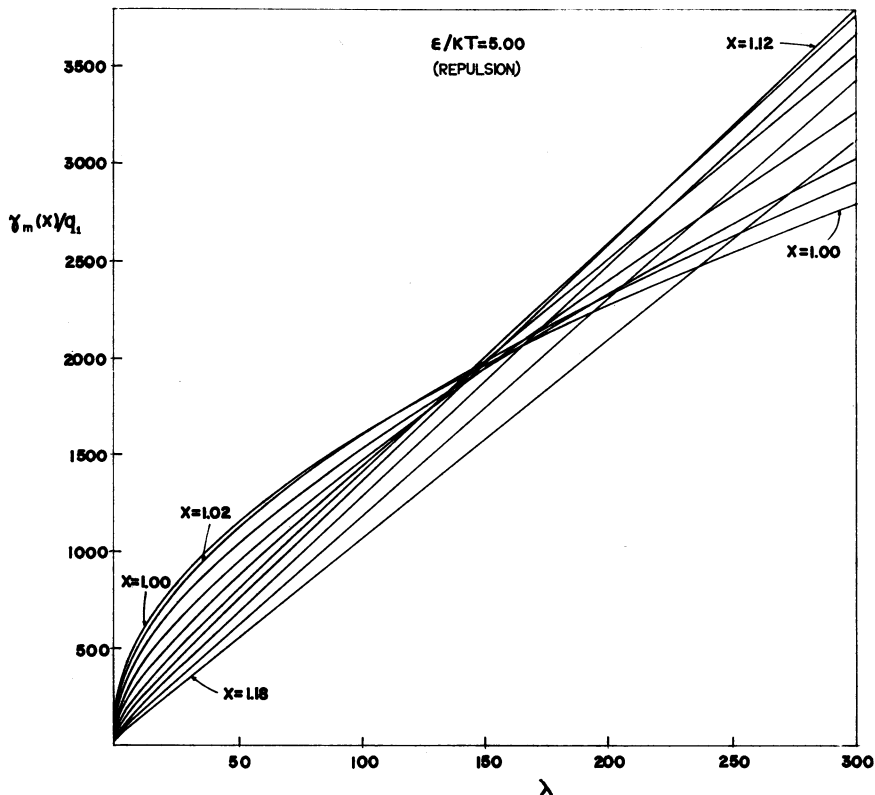


FIG. 7.—The envelope is a plot of $e^{-\mu_1/kT}/q_1$ against $q_2\lambda_2$ for $\epsilon/kT = 5.00$ (repulsion). There is a phase transition at about $\lambda = \lambda_t = 145$.

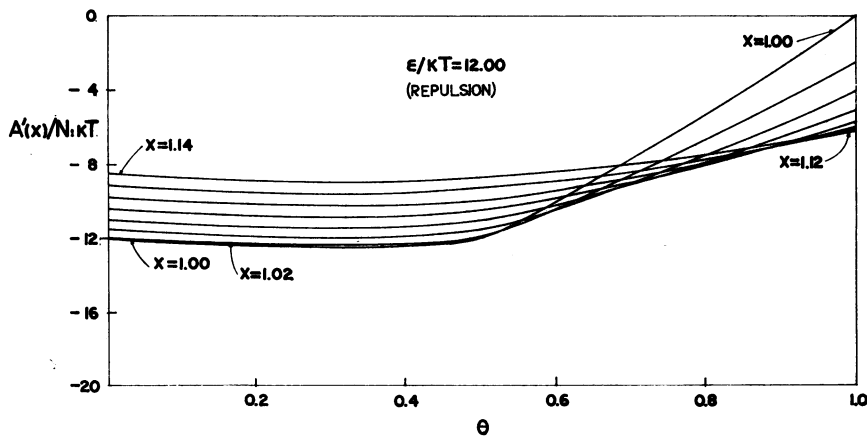


FIG. 8.—The envelope is a plot of the free energy, A'/N_1kT against θ for $\epsilon/kT = 12.00$ (repulsion). The two phases have $\theta \cong 0.50$ and $\theta \cong 1.00$.

Define

$$\bar{z} = \int e^{-w_1(x)/kT} dx, \quad \bar{u} = \frac{1}{\bar{z}} \int e^{-[w_1(x) + w_2(x)]/kT} dx.$$

Then the secular equation is

$$\begin{vmatrix} q_1 \bar{z} - \gamma & q_1 \bar{z} \\ q_1 \bar{z} \lambda & q_1 \bar{z} \bar{u} \lambda - \gamma \end{vmatrix} = 0. \quad (13)$$

This has exactly the form of equation (6), but integration over x has already been carried out. Incidentally, fluctuations in x are large here because \bar{z} and \bar{u} refer to a single unit (not a macroscopic system). Hence we cannot use a single value of x , x^* , as above.

Since equation (13) is of the conventional Ising form, there can be no phase transition ($T_c = 0$).

The last section of Part I is a special case. There are two possible lattice spacings, with $w_1 = w_2 = 0$ or with $w_1 = \epsilon_1$, $w_2 = \epsilon_2$. Thus $\bar{z} = 1 + z$, $\bar{z}\bar{u} = 1 + zu$. With these substitutions in equation (13), we recover equation (I-13).

It was pointed out in Part I that when $u = 1/z^2$, the function $\theta(\lambda, z)$ from equation (I-14) is identical with $\theta(\lambda, z^2)$ from equation (I-8). This follows because \bar{u} in equation (I-14) plays the role of $u = 1/z^2$ in equation (I-8), and

$$\bar{u} = \frac{1 + zu}{1 + z} = \frac{1 + z \cdot z^{-2}}{1 + z} = \frac{1}{z}.$$

* Supported in part by research grants from the Heart Institute of the U.S. Public Health Service and from the National Science Foundation.

† Present address: Division of Natural Sciences, University of California (Santa Cruz).

¹ Hill, T. L., these PROCEEDINGS, 57, 227 (1967).

² Hill, T. L., *Statistical Thermodynamics* (Reading, Mass.: Addison-Wesley Publishing Co., Inc., 1960), chap. 14.

³ Hill, T. L., *Statistical Mechanics* (New York: McGraw-Hill Book Co., Inc., 1956), Appendix 9.