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A NEW STATISTICAL MECHANICAL APPROXIMATION METHOD APPLIED TO THE
TWO DIMENSIONAL HARD SQUARE LATTICE GAS

By

John R. McBride

B.S., Westminster College, Pa., 1968

Presented in partial fulfillment of the
requirements for the degree of

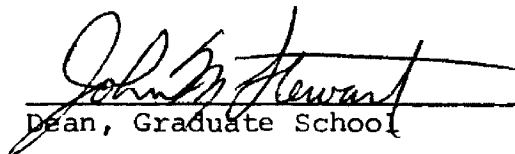
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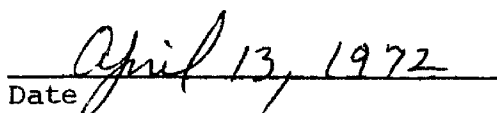
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Chapter 1

INTRODUCTION

In recent years there has been much interest in lattice models which undergo phase transitions. The most famous of these lattice models is the Ising Model of ferromagnetism, which also can serve as a crude model for liquid - vapor transitions. Another interesting model is the hard square lattice gas. This model has been studied in great detail and is found to approximate the solid - liquid phase transition. The hard square lattice gas will be considered in detail in this thesis.

The hard square lattice gas is a two dimensional system of structureless particles confined to a square or rectangular lattice. The occupation of sites on this lattice is determined by a configurational potential energy. This potential is infinite for two particles on the same or nearest neighbor lattice sites and is zero otherwise. Thus the simultaneous occupation of two nearest neighbor sites or the occupation of a single site by more than one particle is forbidden. (See figure 1.1.)

Although the hard square lattice gas does not bear much resemblance to a real physical gas, its use as a model is nonetheless justified. Since the hard square lattice gas is known to undergo a phase transition similar to melting, it could possibly serve as a model for more complex physical phenomena.

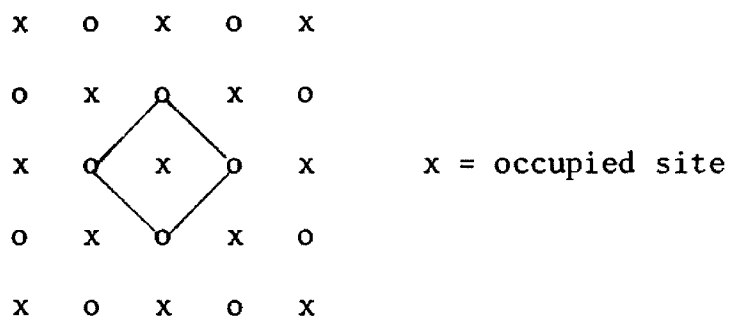


Figure 1.1 -- Closest packed configuration of a hard square lattice gas. (Note that the nearest neighbor exclusions form a square around an occupied lattice site; hence the name "hard square").

In fact it is known that solid argon melts at high temperatures where the interaction between particles is primarily repulsive.¹⁻² This interparticle repulsion is obviously present in the hard square lattice gas.

The hard square lattice gas also resembles various theoretical models which are known to undergo phase transitions. Both the hard sphere and hard disc continuum fluid models undergo a phase transition. Monte Carlo and statistical dynamical calculations confirm this.³⁻⁹ However, because of the extreme mathematical complexity of the problem it has not been solved in complete detail. The hard square lattice gas is the simplest lattice analog of the hard disc continuum fluid. Thus, it would not be beyond belief to expect the phase transition present in the hard square model to resemble that of the continuum fluid since the hard core repulsion is retained in the lattice gas. One should not expect the transitions present in the two models to be identical. However, if the lattice spacing is reduced relative to the radius of the hard disc by excluding further neighbors, one might expect the behavior of the lattice gas to approach that of the

continuum fluid. It has been shown that, at closest packed density, the lattice gas leads to an incorrect asymptotic form for the pressure regardless of the number of lattice sites excluded by the interaction potential.¹⁰ Research in this area is just beginning, however, and much attention will be focused on the behavior of the lattice gas with increased exclusions over the entire range of densities.

A final justification for the use of the hard square lattice gas model is its mathematical tractability. Far more realistic theoretical models have been proposed but in many of these models the mathematical difficulties present preclude an accurate solution. Alder and Wainwright⁶⁻⁹ used hundreds of hours of computer time on an IBM 704 in the classic study of the hard sphere continuum fluid. As a comparison less than one half hour of computer time on an SDS Sigma 7 was necessary to perform the calculations included in this thesis.

HISTORICAL BACKGROUND

The hard square lattice gas was proposed by Domb¹¹ to deal with the theory of melting. Approximate treatments of this problem have been presented by Temperley¹²⁻¹⁴ and Burley.¹⁵⁻¹⁶ Burley used the Bethe approximation while Temperley attacked the problem using the Mayer b_1 and B_1 series. Levesque and Verlet¹⁷ and Jancovici¹⁸ and Stell¹⁹ applied the Percus - Yevick and hypernetted chain approximations to the model. All of the above approximations are known to be unreliable indicators of the nature and location of phase transitions.

The first calculation on the hard square lattice gas which may

be considered "exact" was performed by D.S. Gaunt and M.E. Fisher.²⁰ Gaunt and Fisher based their analysis on a series expansion. They derived the first thirteen terms of the activity and virial series, and the first nine terms of the high density expansion for the pressure. A double series which converges at all densities was also derived. These series were then extrapolated using the Pade and ratio of coefficients methods. Using these methods Gaunt and Fisher were able to conclude that the hard square lattice gas undergoes a continuous order - disorder phase transition at a density of approximately 74 percent of closest packing. The transition activity was $z_{tr} = 3.80$ and the pressure at the transition was $pa^2/kbT = 0.792$. Gaunt and Fisher found that the compressibility exhibits a maximum near the transition; however they concluded, perhaps erroneously, that the compressibility would probably remain finite. It is worth noting that a discontinuous phase transition was found in the hard disc approximation, the continuum analog of this model.

Gaunt and Fisher's calculation included an interesting parameter. They developed an order parameter which is used in signaling the appearance of the phase transition. This order parameter measures the tendency of the lattice to assume an ordered configuration and will be discussed in detail later. The order parameter is an excellent indicator of the precise nature of the phase transition. It is not included in any of the other "exact" calculations.

The hard square lattice gas problem has also been "solved" by Runnels and Combs,²¹⁻²² and Ree and Chestnut²³ using the exact finite method (EFM). The EFM uses a matrix formulation of the problem and

makes use of an electronic computer to carry out the numerous logical and arithmetic operations involved. The lattices used in the EFM are finite in one dimension and infinite in the other. The problem is solved for a sequence of systems of increasing column width. Finally this information is extrapolated to give data for a system infinite in both dimensions.

The matrix approach used in this problem has been developed by several workers and is now well known.²⁴ A brief outline of this method follows. Let us consider a square lattice of L rows and a circumference of M sites which is "wrapped" to form a cylinder eliminating edge effects and giving us a system that is essentially infinite in one dimension as L is made very large. There are a total of $L \times M = V$ lattice sites available. All of the various possible configurations of the lattice can be described by the arrangement of the particles on each of the L rings. The possible states of a ring of M sites can be denoted as $\nu = 1, 2, 3, \dots, x$, recalling that two adjacent lattice sites may not be occupied simultaneously. The states ν take into account only interactions on a single ring. To consider interactions between a pair of rings, a matrix with elements $\alpha(\nu\nu')$ is constructed. $\alpha(\nu\nu')$ is one if ν of ring 1 is compatible with ν' of ring 2, and is zero otherwise. To include the activity a matrix with the following elements is defined:

$$P(\nu\nu') = \alpha(\nu\nu') z^{1/2(n(\nu) + n(\nu'))} \quad 1.1$$

where z is the activity, (at low activities it is asymptotic to the density.) and n_ν is the number of particles in state $\nu = i$. The

essential equations of the matrix formulation are:

$$\sum_{\nu\nu'} z^{\eta(\nu)/2} (P^{1-1})_{\nu\nu'} z^{\eta(\nu')/2} = \sum_n \Omega(x, N) z^n \quad 1.2$$

and
$$\sum_n \Omega(x, N) z^n = \overline{\Xi}(x, z). \quad 1.3$$

The first summation is over all $\nu\nu'$ combinations. $\Omega(x, n)$ is the number of arrangements of N molecules on x sites and $\overline{\Xi}$ is the grand canonical partition function. All of the thermodynamic information for the system can be derived from the grand canonical partition function. Thus we have:

$$\overline{\Xi} = \exp(pv/kt) \quad 1.4$$

and
$$v\rho = \langle n \rangle = z \frac{\partial \ln \Xi}{\partial z} \quad 1.5$$

Here p is the pressure and ρ is a dimensionless number density.

(Maximum density in this case is one half). The matrix method also develops the following useful asymptotic relationship:

$$\ln \Xi = L \ln \lambda_1(M, z) \quad (L \rightarrow \infty) \quad 1.6$$

where $\lambda_1(M, z)$ is the largest eigenvalue of the matrix P. Thus we can also derive all of the thermodynamic information from the largest eigenvalue of the P matrix. Many numerical techniques are available for obtaining this eigenvalue.

Both Runnels and Combs and Ree and Chestnut use group theory to reduce the P matrix thus greatly simplifying their calculation procedure. The interested reader is referred to reference 16 for a description of this method. Ree and Chestnut note that for a cylinder with a circumference of 18 sites the original P matrix is 5778 x 5778 while the

reduced matrix is 209 x 209, a size well within the storage capacity of most modern electronic computers.

The use of the EFM in the solution of this problem indicates that the phase transition takes place continuously without any sharp break in the pressure versus density plot. This phase transition occurs at an activity of $z_{tr} = 3.7996$, a density of 0.7355 (Closest packed density = 1.), and a pressure $p_t/kT = 0.7916$.²³ The compressibility exhibits a maximum near the transition point, however, the compressibility calculated by the EFM appears to become infinite as opposed to Gaunt and Fisher's finite compressibility. Runnels and Combs also report a logarithmic increase in the specific heat maximum which occurs at the point of closest approach to a phase transition for finite systems.

The hard square lattice gas has recently been studied by A. Bellemans and R.K. Nigam.²⁵⁻²⁶ Their main interest was in studying the hard sphere lattice gas problem with other than nearest neighbor exclusions. They performed some calculations on the hard square lattice gas, using three different methods, and their results simply confirm those of previous workers. N. Karayiamis, C.A. Morrison and D. E. Wortman²⁷ also present an "exact" solution to the hard square lattice gas problem. Their calculation procedure was essentially the same as the EFM. In extrapolating to a lattice infinite in two dimensions they use a procedure that is identical with that of Ree and Chestnut. It is worthwhile to emphasize that a phase transition does not occur in systems which are infinite in only one dimension. Results for these systems must be extrapolated to give data for systems that are

infinite in two dimensions, where a phase transition may occur.

PRELIMINARY REMARKS

In this thesis a new method for solving problems in lattice statistics is developed. The utility of this method is demonstrated in the solution of the hard square lattice gas problem. As was noted previously, the hard square lattice gas has been studied thoroughly and "exact" results are available as a useful comparison. Many of the ideas used in developing this method are contained in a recent paper by G.W. Woodbury²⁸⁻²⁹ which in turn draws on the EFM. In this approximation thermodynamic data from two different sized systems are combined together so we shall call it the TSM (Two Systems Method).

Using the TSM permits the calculation of an order parameter as does the method of Gaunt and Fisher.²⁰ (An order parameter is not included in any of the other calculations). To calculate an order parameter we subdivide the square lattice into sublattices as shown in Figure 1.2. For systems of even dimension these sublattices will be equivalent; for odd systems one sublattice will be favored over the other at the high density limit. The order parameter, R , is defined as follows:

$$R = 2 * (|\rho_a - \rho_b|) \quad 1.7$$

where ρ_a and ρ_b are the densities for sublattice A and B respectively. The maximum density of each sublattice is defined to be one half, so at closest packed density, when $\rho_a = \text{one half}$ and $\rho_b = \text{zero}$ (or the other way around) the order parameter is one. When two sub-

lattices are equally occupied then $R = \text{zero}$. The order parameter is quite useful in characterizing the phase transition. As the density is increased the order parameter is apparently zero until the transition is reached and then approaches one in the limit of closest packing.

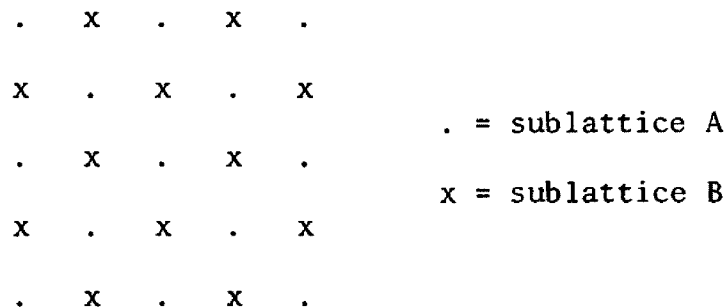


Figure 1.2 -- 5 x 5 lattice showing sublattices. Note that sublattice A has more sites than sublattice B.

It is also possible to calculate a surface tension between the two ordered "phases", A and B, with the TSM. (Phase A preferentially occupies sublattice A, phase B preferentially occupies sublattice B). Woodbury³⁰⁻³¹ has shown that the necessary information for the surface tension calculation is statistical information of phases A and B; this is available with the TSM, a modified EFM, but not through the standard EFM. The surface tension for the hard square lattice gas has been recently calculated by Woodbury²⁹ using a modified EFM procedure, and it appears to be an excellent indicator of the position of the phase transition as the surface tension converges to zero at the point of transition.

Much of the utility of the TSM lies in its rapid convergence. Excellent thermodynamic results are produced in this method more rapidly than with any of the other methods. The combination of a

6 and an 8 column width system with fixed boundaries gives results which are only slightly worse than a $16 \times \infty$ system in the EFM. The complete calculation procedure for the above combination takes approximately four minutes of computer time on a SDS Sigma 7 system, as compared to eighty minutes on an IBM 7040 for the $16 \times \infty$ EFM system. This time savings and corresponding financial gain should make the TSM useful.

Finally the TSM can be expanded to include the problem of other than nearest neighbor exclusions. This problem has been studied recently by several authors but very few definite conclusions have been reached.^{25-26, 32-33} It is apparent, however, that the convergence of some properties to the hard disc continuum fluid is slow. Nevertheless, it is hoped that by systematically increasing the number of excluded lattice sites, characteristics will be discovered which will hold for the hard disc continuum model. The TSM is by no means the only way to proceed in attacking the problem of increased lattice exclusions, however, its rapidity of convergence makes it appear particularly useful.

Chapter 2

DEVELOPMENT OF THE TSM

DERIVATIONS

We shall begin this chapter by studying some preliminary ideas which are necessary in the development of the TSM. There are several types of lattice dimensions to be described here, and they must be carefully distinguished, finite in both dimensions, infinite in both dimensions, and finite in one, infinite in the other. We will now consider this last type. Let us consider a hard square lattice gas with L columns and M rows. Here we take $L \rightarrow \infty$. Let U_i be a variable describing the state of column i . It is well known that the thermodynamic properties of this lattice system can be determined by finding the largest eigenvalue of a matrix with the following elements:

$$P(U, U') = \alpha(U, U') z^{(n(U) + n(U'))/2} \quad 2.1$$

$\alpha(U, U')$ is one if U and U' are compatible and is zero otherwise.

It has been shown that the eigenvector Ψ_1 , corresponding to the largest eigenvalue, λ_1 , of the matrix P is related to the probability distribution for the column states for columns infinitely far from either end. Let $p\{U_i\}$ be the probability that column i ($1 \ll i \ll L$) is in state U_i , and let Ψ_{U_i} be the U_i th component of Ψ_1 . $p\{U_i\}$ and Ψ_1 are related as follows:

$$p\{U_i\} = \Psi_1^2(U_i) \quad 2.2$$

where ψ has been normalized so that

$$\sum_{\psi_i} \psi_1^2 (u_i) = 1. \quad 2.3$$

Since ψ_1 is the eigenvector corresponding to the largest eigenvalue of the matrix P we know that

$$P \psi_1 = \lambda_1 \psi_1 \quad 2.4$$

Thus, if ψ_1 could be approximated or solved for exactly we could obtain λ_1 from equation 2.4 and determine the thermodynamics of the system.

Many numerical schemes are available for determining the eigenvalues and eigenvectors of a matrix. Most of these methods are feasible only with the aid of an electronic computer as the numerical calculations involved are staggering. The situation is much simpler when only the largest eigenvalue and corresponding eigenvector are needed, however, a computer is still necessary for the calculation. Most of these schemes involve iterative techniques. In one such technique the matrix P is applied to an arbitrary vector ϕ many times. It is known that this result approaches the eigenvector ψ_1 corresponding to the largest eigenvalue, λ_1 , unless ϕ and ψ_1 are orthogonal.³⁵ Thus we have:²³

$$\lim_{L \rightarrow \infty} \frac{P^L \cdot \phi}{\lambda_1^L} = a \psi_1 \quad 2.5$$

which is a simple iterative method for obtaining λ_1 and ψ_1 .

Let us now consider the eigenvalue spectrum of the P matrix given in equation 2.1. The P matrix has elements which are obviously

real and it is symmetric; thus it has real eigenvalues, λ_i . All of the elements of P are non-negative and no zeros occur in the first row or column. (Column state u_1 is arbitrarily assigned the completely unoccupied configuration, thus all column states are compatible with u_1 and all other configurations will have at least one lattice site occupied so we will have positive elements for the first row and column of P). This implies that each element of P^2 is positive and hence that P is primitive.³⁶ The largest eigenvalue of a primitive matrix is positive, real, and greater in magnitude than any of the other eigenvalues. Thus we have:

$$\lambda_1 > |\lambda_i| \quad i \neq 1 \quad 2.6$$

for this system of finite M and infinite L . It should also be noted that since the eigenvalue λ_1 of the P matrix is nondegenerate, the eigenvector Ψ_1 is unique except for a constant factor.

We can justify the preceding statements about a one dimensionally infinite system by considering a two dimensionally finite system (L & M finite) and then taking the limit $L \rightarrow \infty$. Consider the probability distribution for column M :

$$P\{u_m\} = \sum_{u_1 \dots u_{m-1}} \phi(u_1) P(u_1 u_2) \dots P(u_{m-1} u_m) \quad 2.7$$

$$\sum_{u_{m+1} \dots u_1} P(u_m u_{m+1}) \dots P(u_{1-1} u_1) \phi(u_1) / \Xi$$

where:

$$\phi(u_1) = \sum_Z n(u_1) / Z \quad 2.8$$

and where the partition function Ξ is given in equations 1.2 and 1.3.

To justify equation 2.7 it is sufficient to start with $p\{u_m\}$

in the form:

$$P\{u_m\} = \sum_{u_1 \dots u_{m-1}} \sum_{u_{m+1} \dots u_1} z^{n(u_1) + \dots + n(u_1)} \frac{e^{-(E(u_1) \dots (u_1) / kt)}}{e} \quad 2.9$$

where $(E(u_1) \dots (u_m))$ is the configurational energy (zero or infinity). Using the function $\alpha(uu')$ introduced in equation 1.1 we

may rewrite equation 2.9 as follows:

$$P\{u_m\} = \sum_{u_1 \dots u_{m-1}} \sum_{u_{m+1} \dots u_1} z^{n(u_1)} \alpha(u_1 u_2) z^{n(u_2)} \dots \alpha(u_{m-1} u_m) z^{n(u_m)} \cdot \alpha(u_m u_{m+1}) \dots \alpha(u_{l-1} u_l) z^{n(u_l)} / \equiv \quad 2.10$$

or:

$$P\{u_m\} = \sum_{u_1 \dots u_{m-1}} \sum_{u_{m+1} \dots u_1} z^{n(u_1)/2} \alpha(u_1 u_2) z^{n(u_2)/2} \dots \quad 2.11$$

$(z^{n(u_{l-1})/2} \alpha(u_{l-1} u_l) z^{n(u_l)/2}) (z^{n(u_l)/2}) / \equiv$
 which is equivalent to equation 2.7. We shall designate the "end vector" given in equation 2.8 as the "Free Boundary" end vector; other conditions may be forced on the boundary by choosing ϕ differently.

Now we shall consider the limit $L \rightarrow \infty$. First replace L in equation 2.7 by $2L + 1$, so the center column is $L + 1$; equation 2.7 then becomes:

$$P\{u_{l+1}\} = (\phi \cdot P^l) u_{l+1} (P^l \cdot \phi) u_{l+1} / \equiv \quad 2.12$$

or in the limit $L \rightarrow \infty$ the center column distribution is:

$$P\{u\} = \lim_{L \rightarrow \infty} (P^l \cdot \phi) u^2 / \equiv \quad 2.13$$

The equation along with equation 2.5 justifies equation 2.2.

As mentioned previously, there is no degeneracy and hence no long range order in the above case ($L = \infty$, M finite).

However, there is strong evidence^{23,38} for an asymptotic degeneracy of the form:

$$\lim_{M \rightarrow \infty} \left| \frac{\lambda_1}{\lambda_2} \right|^m = 1 \quad 2.14$$

and

$$\lim_{M \rightarrow \infty} \frac{\lambda_1}{\lambda_2} = -1 \quad 2.15$$

We shall see below that this will lead to a specific type of long range order.

The above form of the asymptotic degeneracy leads to alternating column distributions in the interior of a system in which L and M are of the same order of magnitude and both very large. To see this, we shall first expand our end vector ϕ in terms of the eigenvectors of the matrix P. Thus:

$$\phi = a \psi_1 + b \psi_2 + \dots \quad 2.16$$

If we iterate M times with this trial vector on the P matrix we will obtain the result:

$$\frac{P^M \phi}{\lambda_1^M} = a \psi_1 + b \left(\frac{\lambda_1}{\lambda_2} \right)^m \psi_2 + \dots \quad 2.17$$

Quantities beyond ψ_2 are not significant since only the largest and smallest eigenvalues λ_1 and λ_2 are almost equal in magnitude and opposite in sign, and no other degeneracies occur. If we take a system in which $L = 2M + 1$, the probability distribution for the column states of the center column is, according to equation 2.13,

$$P\{u\} \propto [a\psi_1 + b \left(\frac{\lambda_1}{\lambda_2} \right)^m \psi_2]^2 \quad 2.18$$

Thus we see that the probability distribution for the column states depends on the quantity $\left(\frac{\lambda_1}{\lambda_2} \right)^M$. From equations 2.16 and 2.17 we note:

$$\left(\frac{\lambda_1}{\lambda_2} \right)^m = \pm 1 \quad 2.19$$

depending on whether M is odd or even. Thus the column neighboring the center column has the distribution

$$P\{u\} \propto \left[a \psi_1 + b \frac{(\lambda_1)^{m-1}}{(\lambda_2)} \psi_2 \right] \left[a \psi_1 + b \frac{(\lambda_1)^{m+1}}{(\lambda_2)} \psi_2 \right] \quad 2.20$$

or

$$P\{u\} \propto \left[a \psi_1 - b \frac{(\lambda_1)^m}{(\lambda_2)} \psi_2 \right]^2 \quad 2.21$$

which differs from equation 2.18 for the center column by a sign.

For the interior columns the sign alternates from column to column.

Our iterative scheme is amended as follows to include the idea of alternating column probability distribution functions. We apply the matrix P to our end vector ϕ a fixed number of iterations, the number being proportional to M. The resulting vector is related to the probability distribution for the column states, however, now at high activity we have alternating column probability distribution functions. Thus, instead of equation 2.2 we have the following relations:

$$P\{u_i\} = \Theta^2 (u_i) \quad i \text{ odd} \quad 2.22$$

and

$$P\{u_i\} = \chi^2 (u_i) \quad i \text{ even} \quad 2.23$$

where Θ and χ are the alternating vectors.

If we apply an even number of iterations to the matrix P we have:

$$\frac{P^m \cdot \phi}{\lambda_1^m} = \chi \quad M = \text{even} \quad 2.24$$

and iterating once again we have:

$$\frac{P^{m+1} \cdot \psi}{\lambda_1^{m+1}} = \Theta \quad M + 1 = \text{odd} \quad 2.25$$

Thus far in our discussion we have only considered briefly the importance of the end vector ϕ . Initially in our development, the

choice of the end vector was completely arbitrary, except that ϕ and ψ_1 must not be orthogonal. Later in equation 2.8 we chose ϕ to have the free boundary form so that we would have the normal form for the partition function. The end vector ϕ can be used to influence our system as can be seen in equations 2.16 - 2.18. As we noticed previously for systems of odd finite dimension ($M = \text{odd}$, $L = \text{odd}$), one sublattice is favored over the other in the high density limit. (One sublattice has more sites than the other). The system will tend to form a closest packed configuration on the favored sublattice so that an order parameter may be calculated. With systems of even dimension there is no favored sublattice however. In this case the end vector must be used to favor one sublattice.

By choosing a specific end vector we can "order" the left and right boundaries of our two dimensionally finite system. Let us again consider our iterative procedure. For the end column of our two dimensionally finite system we know:

$$\phi(u_1) \cdot (P^{L-1} \phi)_{u_1} \propto \phi(u_1) \cdot \psi_1(u_1) \propto P\{u_1\} \quad 2.26$$

If we choose the following trial vector:

$$\begin{aligned} \phi(u_i) &= 0 && \text{all states but closest packed} && 2.27 \\ \phi(u_i) &= \delta && \text{closest packed configuration} && \end{aligned}$$

We see that the choice of an end vector can indeed force one sublattice to be favored over the other. We shall designate the above end vector to be the fixed boundary vector. Although the fixed boundary vector is particularly useful in systems of even dimension, it may be similarly used in odd systems. The choice of trial vector also affects the rate of convergence of the iterative procedure.

The "fixed" boundary trial vector forced convergence of the largest eigenvalue faster than any of the trial vectors studied. In the remaining development we will consider only the fixed boundary trial vector.

Thus far in our development we have considered an iterative procedure which handles only a single finite system. Because of limitations in computer storage this system had to be quite small; in fact the largest system studied had a column width of eight ($M = 8$). It is thus easy to assume that the small size of our systems would present problems in extrapolation, as the phase transition we wish to study is assumed to occur only in systems that are infinite in two dimensions. Our problem is thus one of scaling. We are interested in the behavior of the thermodynamic properties in the interior of very large systems, however, the size of these systems make them very difficult to study. We must, therefore, replace these large systems with systems of much smaller dimensions. The dimensions of these small systems are completely arbitrary and are mainly a matter of convenience, however, we must be able to extrapolate these results to a lattice of infinite dimensions.

Let us consider a system of dimension M by $2M + 5$. The left and right ends of this system are "fixed" so as to produce preferential occupation of sublattice A (See figure 1.2) at high activity. (This may be accomplished by iterating with a fixed boundary trial vector). Let us suppose that we calculate the thermodynamic properties of a center column of this system; we will obtain a result quite unlike that of the large system because of the effect of the fixed ends of

the system. In order to cancel out these boundary effects we increase the length of our system by four columns and the width by two rows (increase M by 2) and we calculate the increase in the various thermodynamic properties of the center column. We obtain the probability distributions for the center columns as follows. For the smaller system:

$$P \{u_i\} \propto (P_{(m)}^{m+2} \cdot \phi)^2 u \quad 2.28$$

and for the larger system,

$$P \{u_i\} \propto (P_{(m+2)}^{m+4} \cdot \phi)^2 u \quad 2.29$$

Since we are studying the increase in the various thermodynamic properties upon increasing the column size we obviously need information from two different sized systems (TSM) which must be stored for use in the various combination equations.

We shall first develop an equation for the column density. We recall that for the alternating vectors,

$$P \{u_i\} = \theta^2 (u_i) \quad i \text{ odd}, \quad 2.30$$

$$P \{u_i\} = \chi^2 (u_i) \quad i \text{ even} \quad 2.31$$

These equations correspond to equation 2.2 with the concept of alternating column probability distributions included. As the first step in obtaining a total density P_t we multiply each element of the probability distribution function by its corresponding number density per site $n(u)$ and sum over all states for the nonalternating distributions:

$$P_t = \sum_u \psi^2 (u) \cdot n(u) \quad 2.32$$

or including the alternating column probability distribution concept,

$$\sum_u \psi^2 (u) n(u) + \sum_u \chi^2 (u) n(u) \quad 2.33$$

By using the TSM concept we will get a final expression for the average column density as:

$$P_t = [M+2 (P_t(m+2)) - M (P_t(m))] \cdot 1/2 \quad 2.34$$

The sublattice densities can be calculated in a similar manner. Each column is divided into alternating x and z sites. (See figure 2.1). Note that the x sites belong to sublattice A in the θ distribution and to sublattice B in the χ distribution. The following equations are derived for the sublattice densities. We have for the x and z sites:

$$P_x (\theta \text{ or } \chi) = \sum_{\nu} \eta_{\nu}^2 n_x (\nu) \quad 2.35$$

$$P_z (\theta \text{ or } \chi) = \sum_{\nu} \eta_{(\nu)} n_x (\nu) \quad 2.36$$

where $n_x(\nu)$ for example is the number of particles on x sites divided by M. η_{ν}^2 may be either θ_{ν}^2 or χ_{ν}^2 . The sublattice densities are:

$$P_a = [P_x (\chi) + P_z (\theta)] \cdot 1/2 \quad 2.37$$

$$P_b = [P_z (\chi) + P_x (\theta)] \cdot 1/2 \quad 2.38$$

The quantities P_a and P_b given above are then substituted into analogs of equation 2.34 for final sublattice densities. The order parameter concept fits in quite well here as

$$R = 2 \cdot (|P_a - P_b|) \quad 2.39$$

It is interesting to note that it is because we are using the alternating probability distribution functions that we can calculate an order parameter and sublattice densities. In the EFM average column densities are obtained through differentiation and sublattice densities cannot be obtained at all.

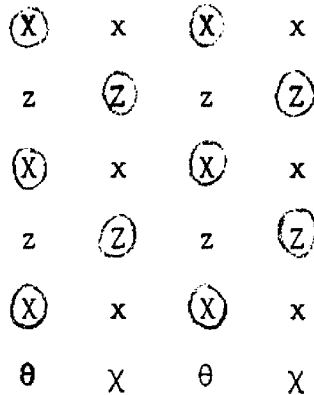


Figure 2.1 -- Figure 2.1 shows x and z sites, circled sites are sublattice A sites. (See figure 1.2).

The pressure for this system can be obtained quite easily. We recall that the pressure is related to the grand canonical partition function as,

$$Ln \Xi = PML / kT \tag{2.40}$$

which in turn can be related to our largest eigenvalue λ_1 :

$$\lim_{M \rightarrow \infty} \lim_{L \rightarrow \infty} \frac{1}{LM} Ln \Xi = \frac{1}{M} Ln \lambda_1(M) = P/kT \tag{2.41}$$

However, in our calculations L and M are not large, so the above equation may be of dubious accuracy because of the effect of the boundary in our system.

In an attempt to cancel out end effects, let us assume the following dependence of λ_1 on M:

$$Ln \lambda_1(M) \approx M Ln \alpha + B \tag{2.42}$$

where α and β are independent of M and β is ascribed to edge effects. From equation 2.41 P/kT is identified as $Ln \alpha$ so equation 2.42 gives us:

$$Ln \lambda_1(M) - B \tag{2.43}$$

We can obtain the pressure from this equation by using the TSM principle to compare two different sized systems:

$$\frac{(M+2) P}{kT} - \frac{(M)P}{kT} \approx \text{Ln } \lambda_1(M+2) - \text{Ln } \lambda_1(M) \quad (M) \quad 2.44$$

or

$$\frac{P}{kT} \approx [\text{Ln } \lambda_1(M+2) - \text{Ln } \lambda_1(M)] 1/2 \quad 2.45$$

We use equation 2.45 to obtain the pressure in our calculations.

Various other thermodynamic properties are also useful in the study of the hard square lattice gas. In particular the isothermal compressibility and the constant pressure heat capacity are extremely useful in determining the position and nature of the phase transition. The compressibility and heat capacity are determined by differentiation as follows:

$$\beta kT = \left(\frac{1}{P_t} \right)^2 z \left(\frac{dP_t}{dz} \right) \quad 2.46$$

and

$$\left(\frac{C_p}{k} \frac{1}{LM} \right) - 1 = \left(\frac{1}{P_t} \right)^3 \left(\frac{P}{kt} \right)^2 z \left(\frac{dP_t}{dz} \right) \quad 2.47$$

Here β is the isothermal compressibility, C_p is the constant pressure heat capacity and L and M are lattice dimensions. (dP_t/dz) is determined by numerical differentiation; the exact methods will be discussed in detail later.

Finally the TSM may be used to calculate a surface tension. Here we use two different equations developed by Woodbury³¹ and Clayton and Woodbury³⁷. Both of these equations use statistical information which is readily available with the TSM. The equations used in the calculation of the surface tension between ordered

phases on sublattices A and B are:

$$\frac{\sigma}{kT} = \frac{1}{2M} \sum_{\nu} (p_a\{\nu\} - p_b\{\nu\}) \ln p_a\{\nu\} \quad 2.48$$

or

$$\frac{\sigma}{kT} = -\frac{1}{M} \ln \sum_{\nu} p_a\{\nu\}^{1/2} p_b\{\nu\}^{1/2} \quad 2.49$$

To reduce end effects in the surface tension, we proceed as in the case of the density and arrive at an equation similar to equation 2.34.

$$\sigma T = [(M+2) \sigma (M+2) - (M) \sigma(M)] \cdot 1/2 \quad 2.50$$

As we noted previously the surface tension for the hard square lattice gas has been recently calculated using a similar method²⁹ and the results appear to be very useful as a phase transition indicator.

The TSM is used to calculate the thermodynamic properties of a series of lattice systems. These results are then extrapolated to produce thermodynamic data for our infinite system. Although we have dealt with only small systems the results we have obtained are quite gratifying. Our results compare very favorably with the exact results which have been previously published. We shall discuss the results of the TSM in detail in the following chapter.

Chapter 3

RESULTS OF THE TSM

DESCRIPTION OF THE TSM PROGRAM

The entire TSM calculation is contained in a single computer program. Input data for this program include the various possible column states, U_i , of the two systems in the calculation, the necessary end vectors, the various activity values to be used, and the number of iterations to be performed before abstracting the thermodynamic data. The TSM computer program is designed to be as general as possible in operation. There are no restrictions on the size of the system, type of trial vector, or number of iterations. The TSM program first calculates the P matrix from the activity and the vectors corresponding to the various column states. The program next iterates a specific number of times with the end vector, normalizing after each iteration and finally obtains the χ and θ vectors. These vectors are then converted to probability distributions and substituted into equations 2.34 - 2.38 to obtain the lattice and sublattice densities. The order parameter is obtained from equation 2.39 and the pressure from 2.45. The P_t versus z isotherm is differentiated numerically to obtain the isothermal compressibility and the constant pressure heat capacity. Finally the surface tension is obtained using equations 2.48 - 2.50. The program continues operation until the thermodynamics have been calculated for all of the input activity values. A copy of the TSM computer program is

included in Appendix I.

CALCULATIONS AND RESULTS

The first calculations attempted with the TSM were performed using the "free" boundary end vector. In order to favor one sublattice over the other at high activity, calculations were attempted only on systems of odd dimension (M odd). The reader will recall that in systems of odd dimension one sublattice has more lattice sites than the other. Thermodynamic data was obtained for lattice systems with a column width of 1, 3, 5, and 7 lattice sites. These data were abstracted after M iterations on an M column width system. The number of iterations performed in this method is quite arbitrary; M was chosen mainly as a matter of convenience. These data were then combined using the TSM to obtain the thermodynamics of the 1 - 3, 3 - 5, and 5 - 7 combination systems. The activities studied ranged from 10^{-6} to 500. Calculations were performed at activities from 0.1 to 10.0 in steps of 0.1 so that the appropriate numerical differentiation could be performed. Thermodynamic data obtained for each activity value include the density, order parameter, pressure, constant pressure heat capacity, and the isothermal compressibility. No surface tension was obtained for the free boundary method.

Figure 3.1 shows a plot of density (P_t) versus activity (z) for the 3 - 5 free boundary combination system. The other free boundary combination systems exhibit similar curves. Figure 3.2 is an expanded graph showing the transition region of the P_t versus z curve for the

1 - 3, 3 - 5, and 5 - 7 combination systems. On the expanded graph we observe that there is a change in the slope of the P_t versus z isotherm as we increase the size of our systems. This behavior is much more clearly exhibited when we differentiate the P_t versus z curve to obtain the isothermal compressibility and the constant pressure heat capacity. The change in slope is an indication of the limit of infinite size. The ideal gas limiting behavior is shown in figure 3.3. In this limit $z = P_t$.

z	P_t	R
.000001	.00000100	.00000000
.0001	.00010012	.00000001

Figure 3.3 -- Ideal Gas Limiting Behavior

In figure 3.4 we plot order parameter versus density (P_t). In this graph we obtain the first indication to the position of the phase transition. We see that as we pass the region of phase transition the order parameter increases sharply to its maximum value of one. The order parameter has a value of zero at $P_t = 0$; it increases slightly then decreases again to a minimum just before the region of phase transition. A plot of this order parameter minimum versus $1/N$ where N is the maximum column width of the combined system (i.e. 1 - 3 $M = 3$, 3 - 5 $M = 5$...) could possibly be extrapolated to give a value for the density at the point of phase transition. Figure 3.5 gives such a plot, however, only three systems have been calculated and

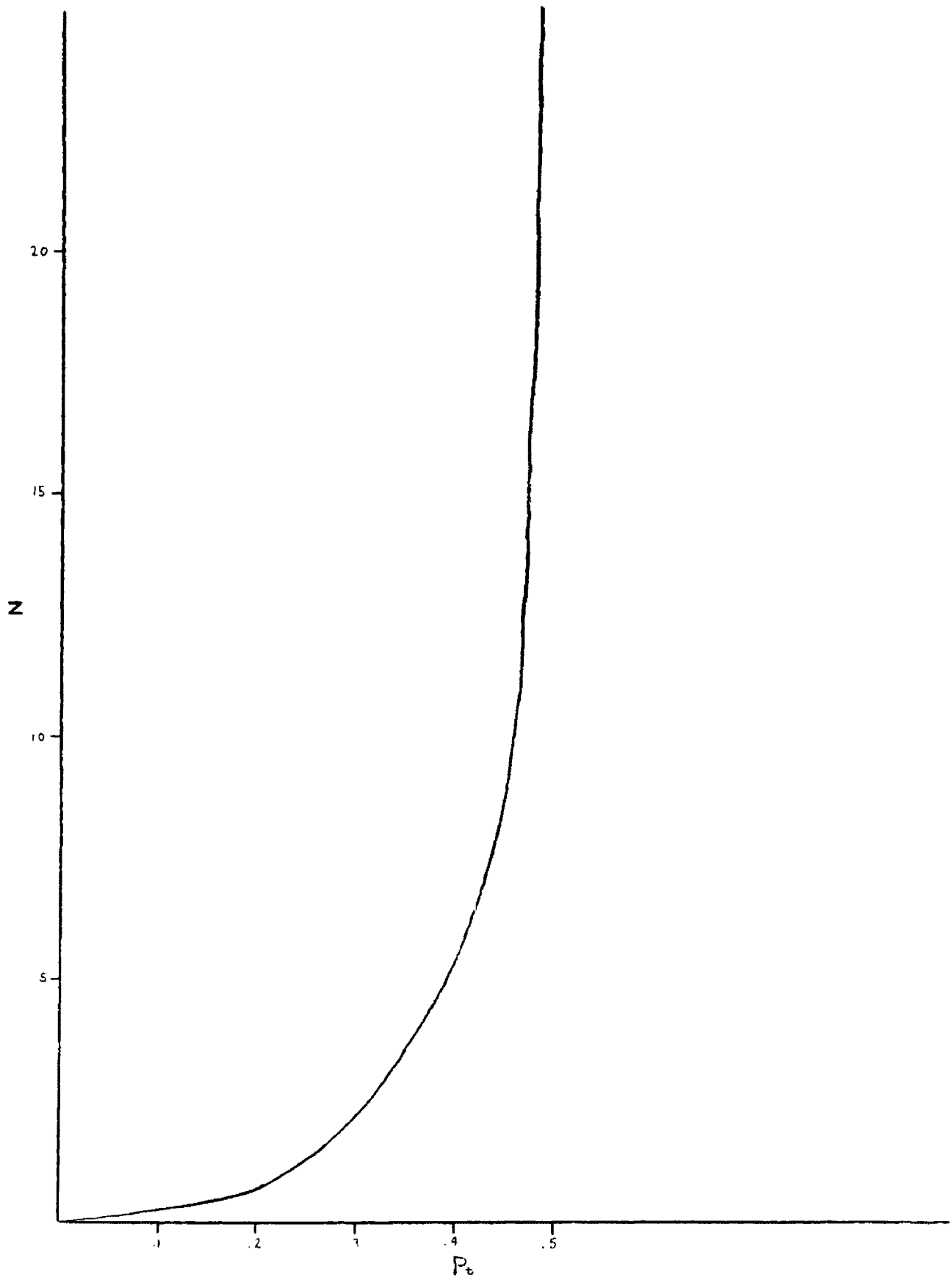


Figure 3.1
Activity vs. Density 3-5 Free Boundary System

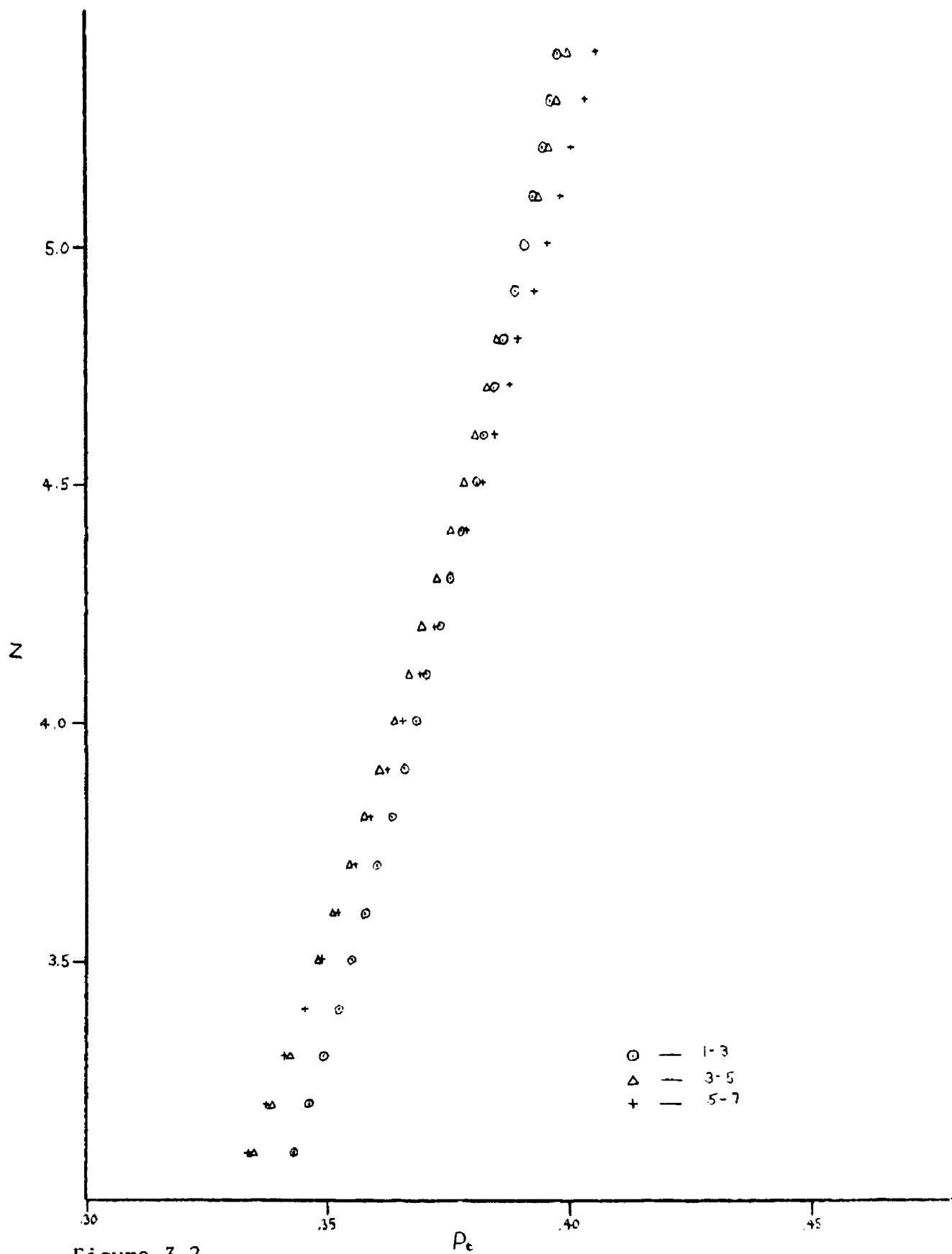


Figure 3.2 Activity vs. Density 1-3, 3-5, 5-7 Free Boundary System

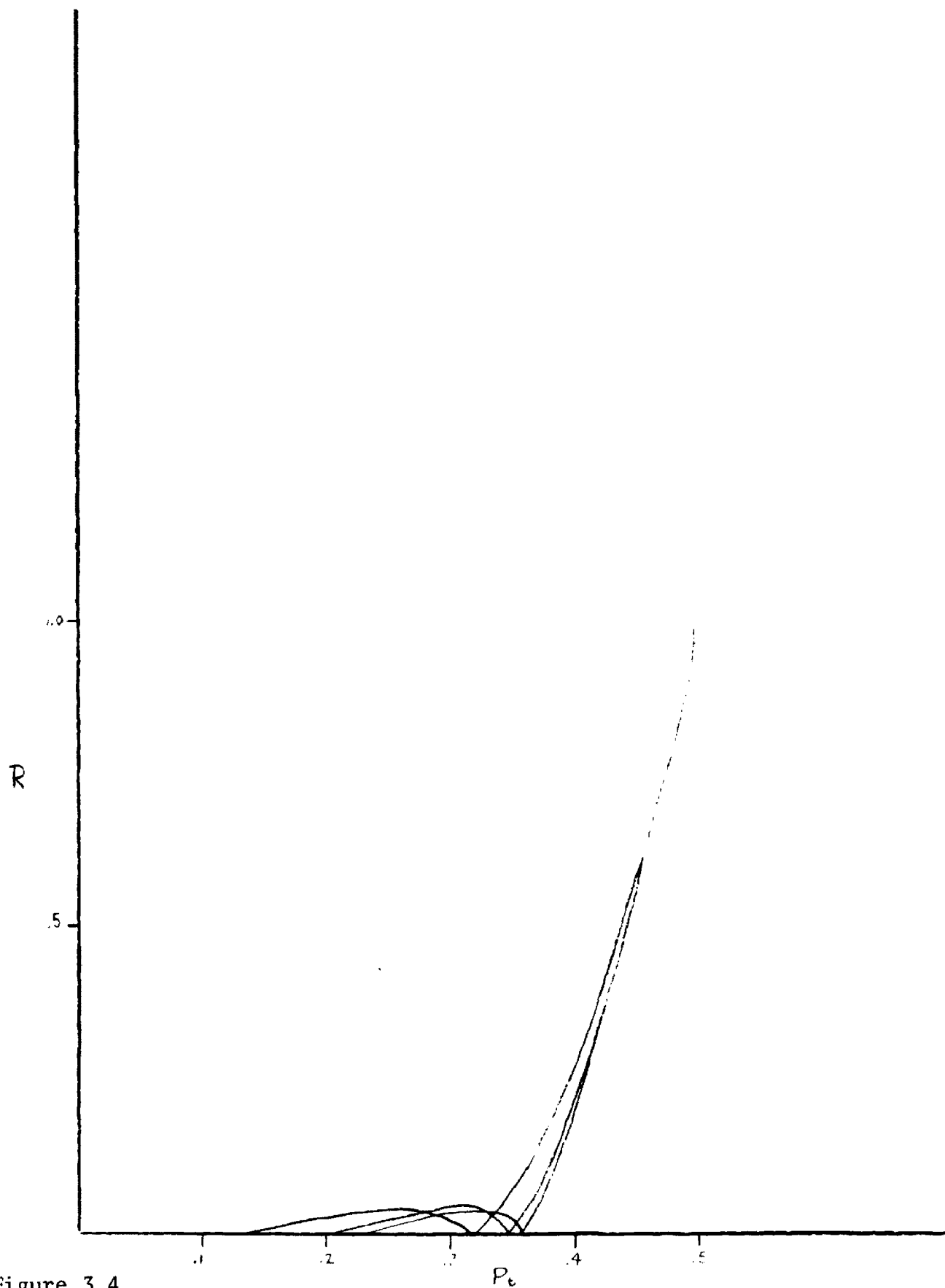


Figure 3.4
Order Parameter vs. Density Free Boundary

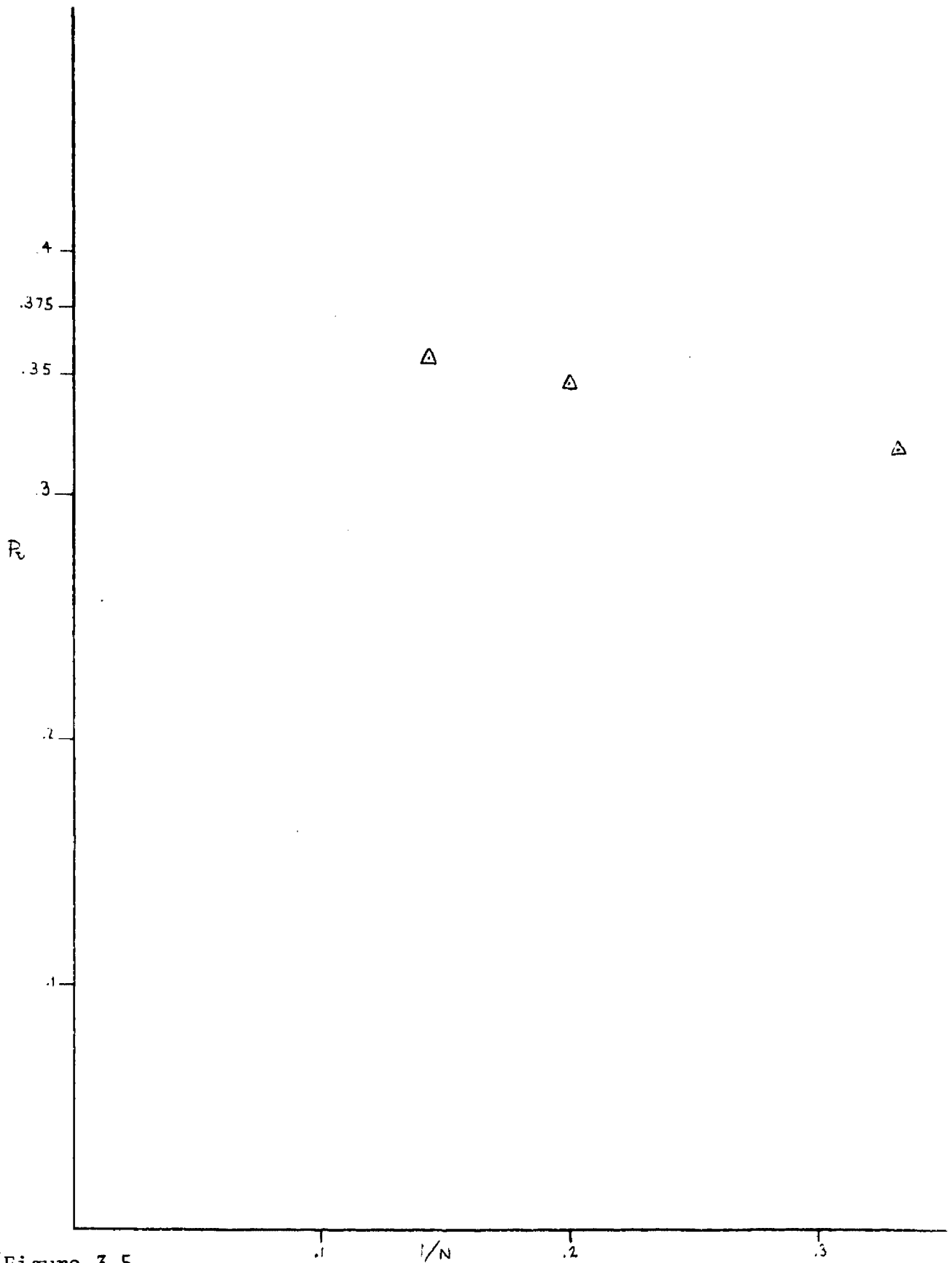


Figure 3.5
Order Parameter Minimum vs. $1/n$ Free Boundary

extrapolation may be meaningless. The three points appear to be converging in the right density region in any case ($P_{tr} = .370$).

One of the major variable factors in the TSM calculation is the number of iterations to be applied to the P matrix. As we observed in Chapter Two, since we are working with finite systems we will lose the alternating behavior of our column probability distribution functions before we obtain convergence of the largest eigenvalue. Thus, we must arbitrarily stop our iterative procedure at some certain point if we wish to calculate an order parameter. In our free boundary calculations we have stopped our iterative procedure after M iterations on an M column width system. Figure 3.6 shows the effect of increasing the number of iterations by a factor of five. The unphysical "hump" in the order parameter versus density plot is removed but the rapid increase in order parameter is shifted to a region of higher density. By increasing the iterations by another factor of five one might expect an order parameter plot resembling the dotted curve in figure 3.6. Of course by iterating to convergence for the largest eigenvalue at all activity values the order parameter would remain zero. The reader will recall that the other thermodynamic properties of the lattice systems are obtained from the largest eigenvalue of the P matrix thus it is mandatory that our iterative procedure converge rapidly to this largest eigenvalue. Fortunately we were able to obtain this rapid convergence. The largest eigenvalue is simply the constant required to normalize the eigenvector which we obtain

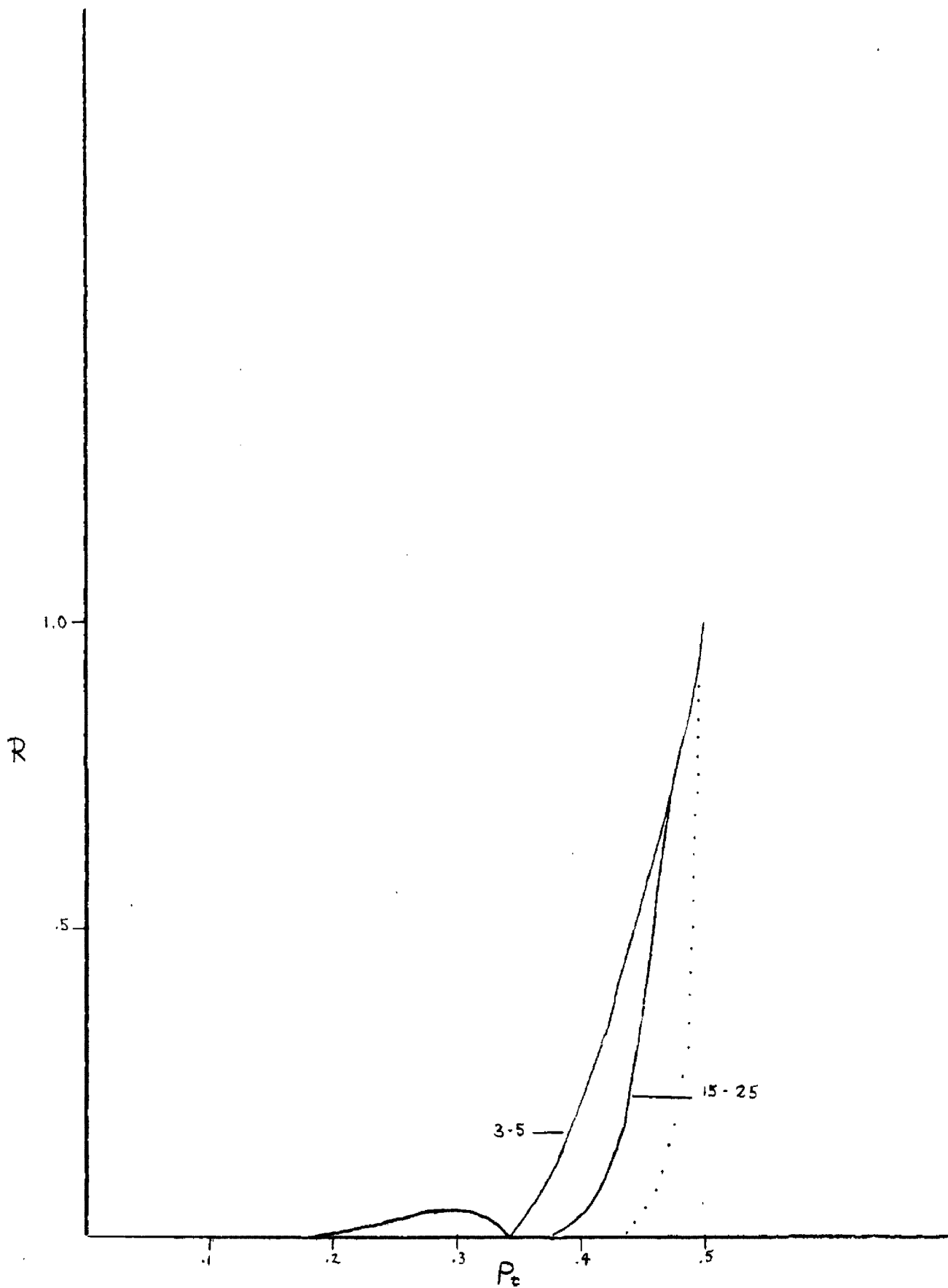


Figure 3.6
Order Parameter 3xn - 5xn System Free Boundary

from our iterative calculation and experience has shown that this constant converges extremely rapidly.

Pressure versus density for the free boundary system is shown in figure 3.7. The graph shown as a dotted line is the exact result of Ree and Chestnut. The plotted results appear to approach the exact result as we increase M. The point of phase transition is indicated by an abrupt change in the slope of the isotherm. Ree and Chestnut predict this point to be $P/kT = 0.7916 \pm 0.0001$.

The constant pressure heat capacity and the isothermal compressibility are calculated by numerically differentiating the P_t versus z isotherm. The validity of numerical differentiation is an open question in any context, however, its use here may be justified in that we are able to reproduce the results obtained in the "exact" solutions. Input errors are reduced since all of the data points are exact rather than calculated from a collocation polynomial. Several numerical methods were studied,³⁹⁻⁴² the method finally used was based on Newton's forward difference polynomial approximation.⁴²

Newton's forward difference polynomial may be stated as:

$$P(k) = y_0 + \binom{k}{1} \Delta y_0 + \binom{k}{2} \Delta^2 y_0 + \dots + \binom{k}{n} \Delta^n y_0 \quad 3.1$$

where $\binom{k}{n}$ is a binomial coefficient. This formula is then differentiated to produce derivatives relative to the argument x using the relation $x = x_0 + kh$. The result of this differentiation is:

$$P'(x) = \frac{1}{h} \left[\Delta y_0 + (k-1/2) \Delta^2 y_0 + \frac{3k^2-6k+2}{6} \Delta^3 y_0 + \frac{2k^3-9k^2+11k-3}{12} \Delta^4 y_0 \right] \quad 3.2$$

$p(x)$ was calculated using differences through order four and

$h = 0.1$.

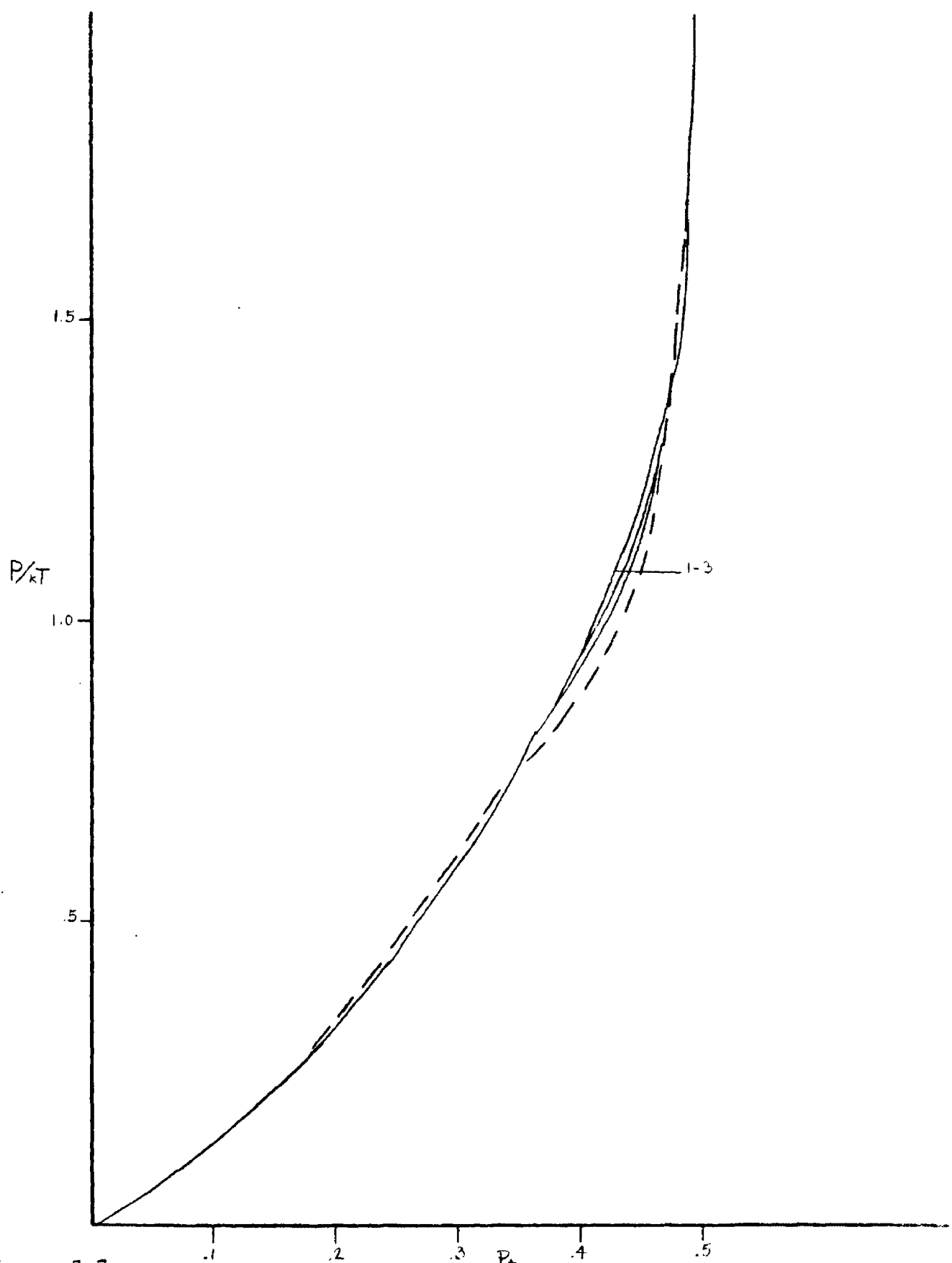


Figure 3.7
Pressure vs. Density Free Boundary

Figure 3.8 is a plot of the isothermal compressibility versus density for the free boundary system. As we increase M the shape of the graph changes, and we begin to observe a "hump" in the graph. These curves appear to have the same form as the "exact" curves of the various authors. Heat capacity versus density for the free boundary system is shown in figure 3.9. We observe an increase in the maximum of the heat capacity curves as we increase M . In figure 3.10 the specific heat maximum is plotted against the logarithm of the column width, N . Again only three points are plotted; however, these results are in agreement with those of Runnels and Combs which indicate an asymptotic linear relationship. This relationship indicates that the specific heat becomes infinite in the limit of a very wide lattice.

TSM calculations were also performed using the "fixed" boundary trial vector. Since the trial vector is used to order the boundaries of our system we studied systems of even dimension (M even). Thermodynamic data was obtained for systems with a column width of 2, 4, 6, and 8 lattice sites. We abstracted this data after $M + 2$ iterations for an M column width system in an attempt to obtain better convergence of the largest eigenvalue. These data were combined using the TSM to obtain the thermodynamics of the 2 - 4, 4 - 6, and 6 - 8 combination systems. Thermodynamic information calculated included all that calculated with the "free" boundary trial vector; in addition a surface tension was calculated.

The order parameter for the fixed boundary system is shown in figure 3.11. Figure 3.12 is a plot of the order parameter minimum versus $1/N$. We see that these three points may be extrapolated to

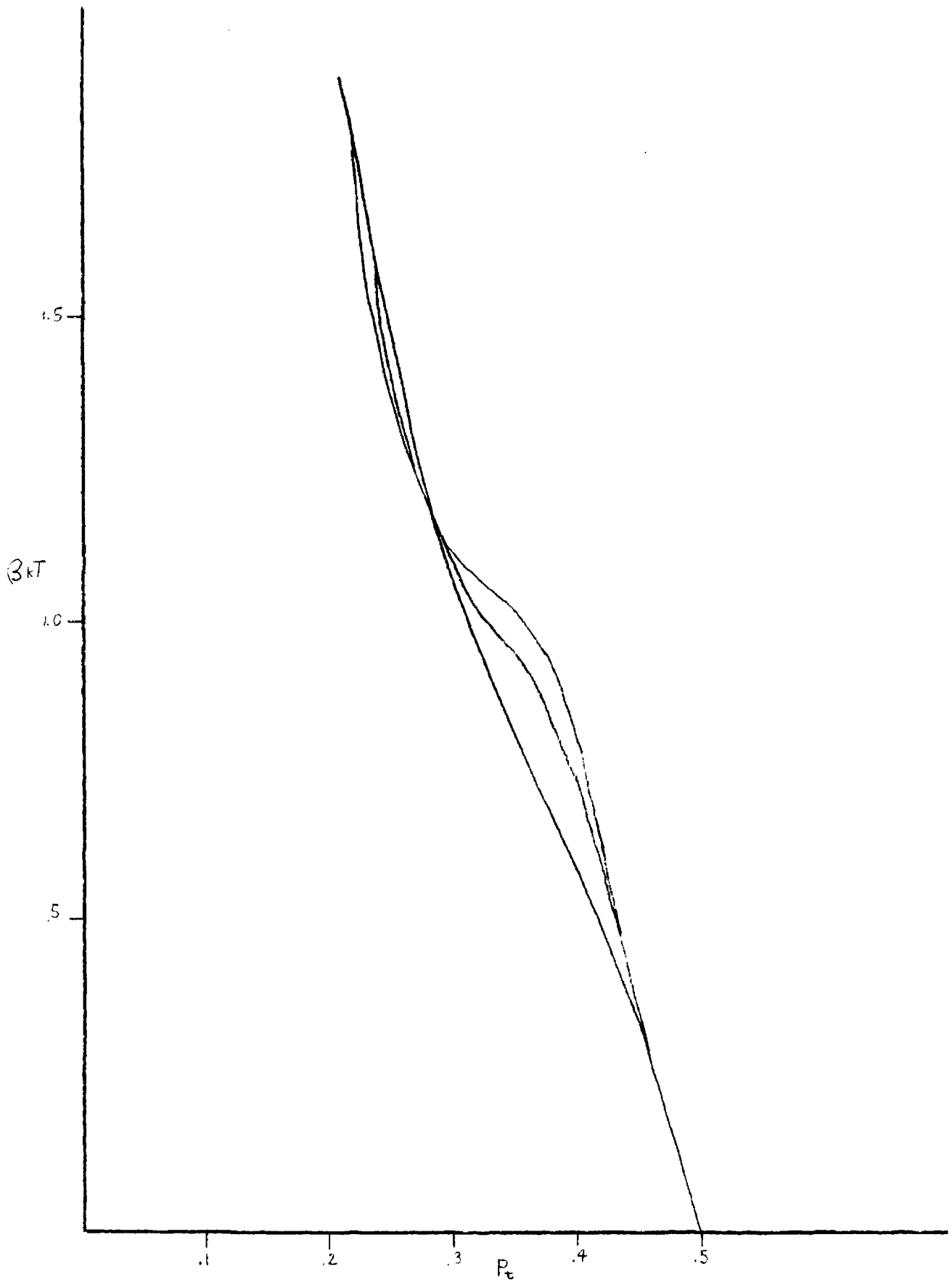


Figure 3.8
Compressibility vs. Density Free Boundary

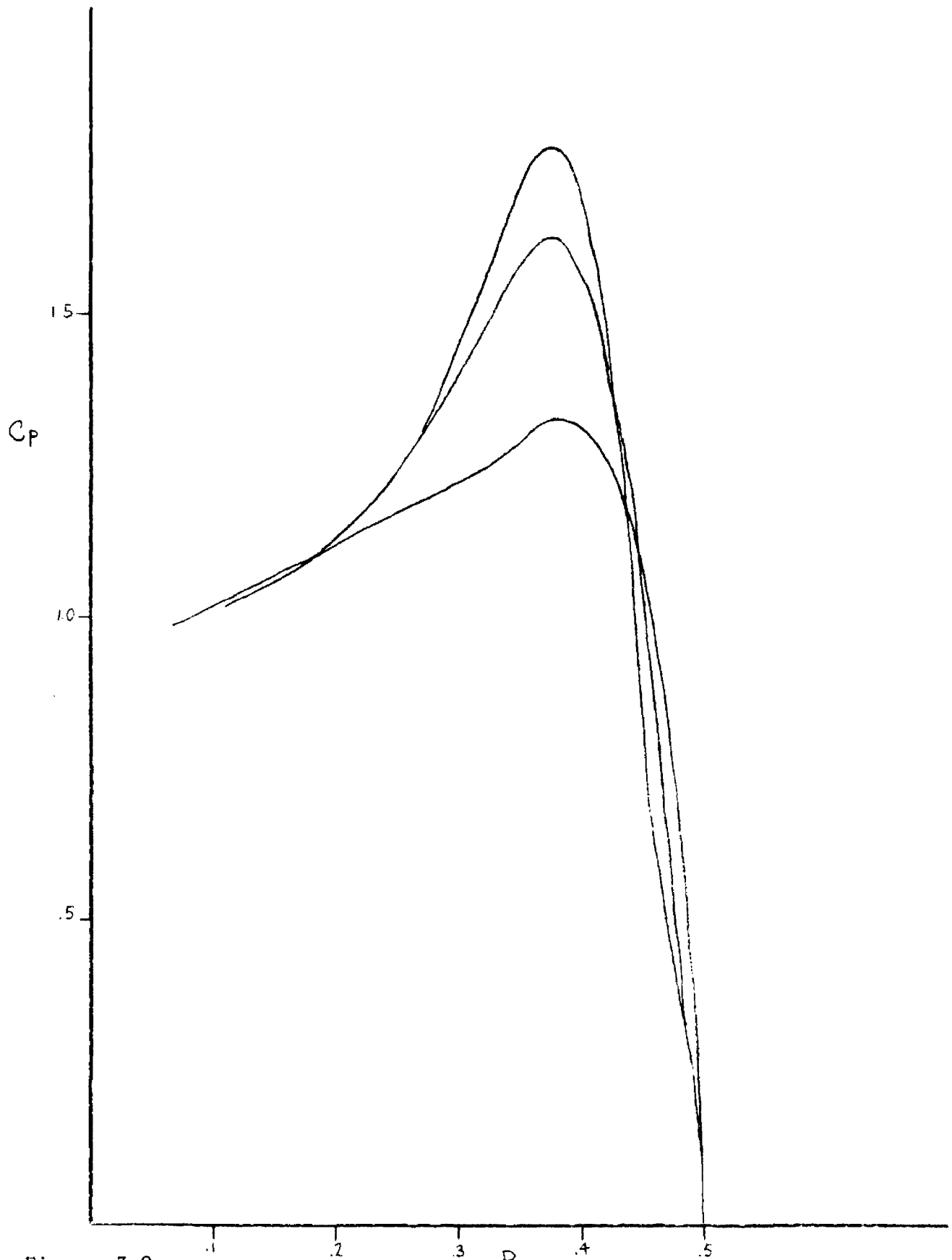


Figure 3.9
Heat Capacity Vs. Density Free Boundary

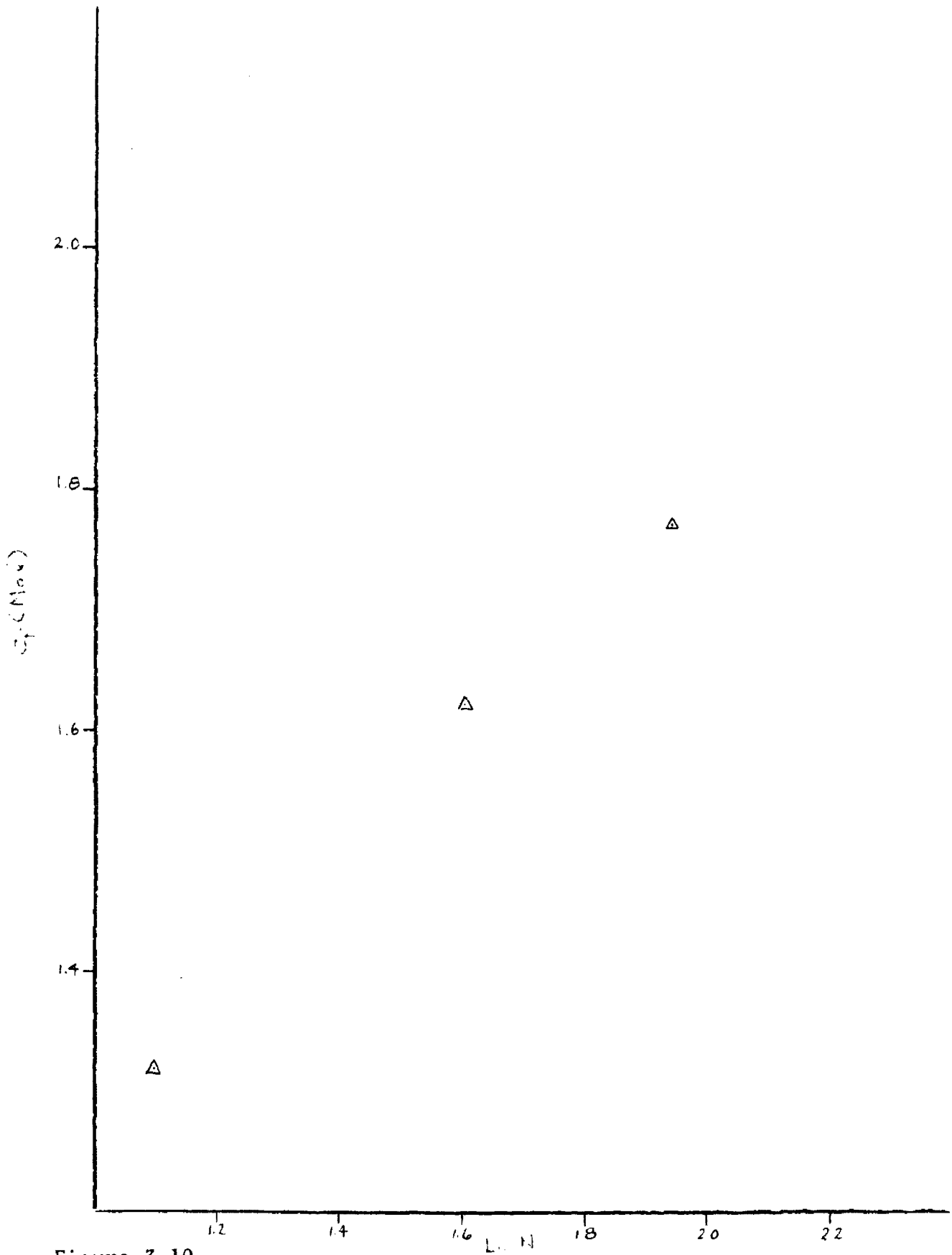


Figure 3.10
Heat Capacity Maximum Vs. Log N Free Boundary System

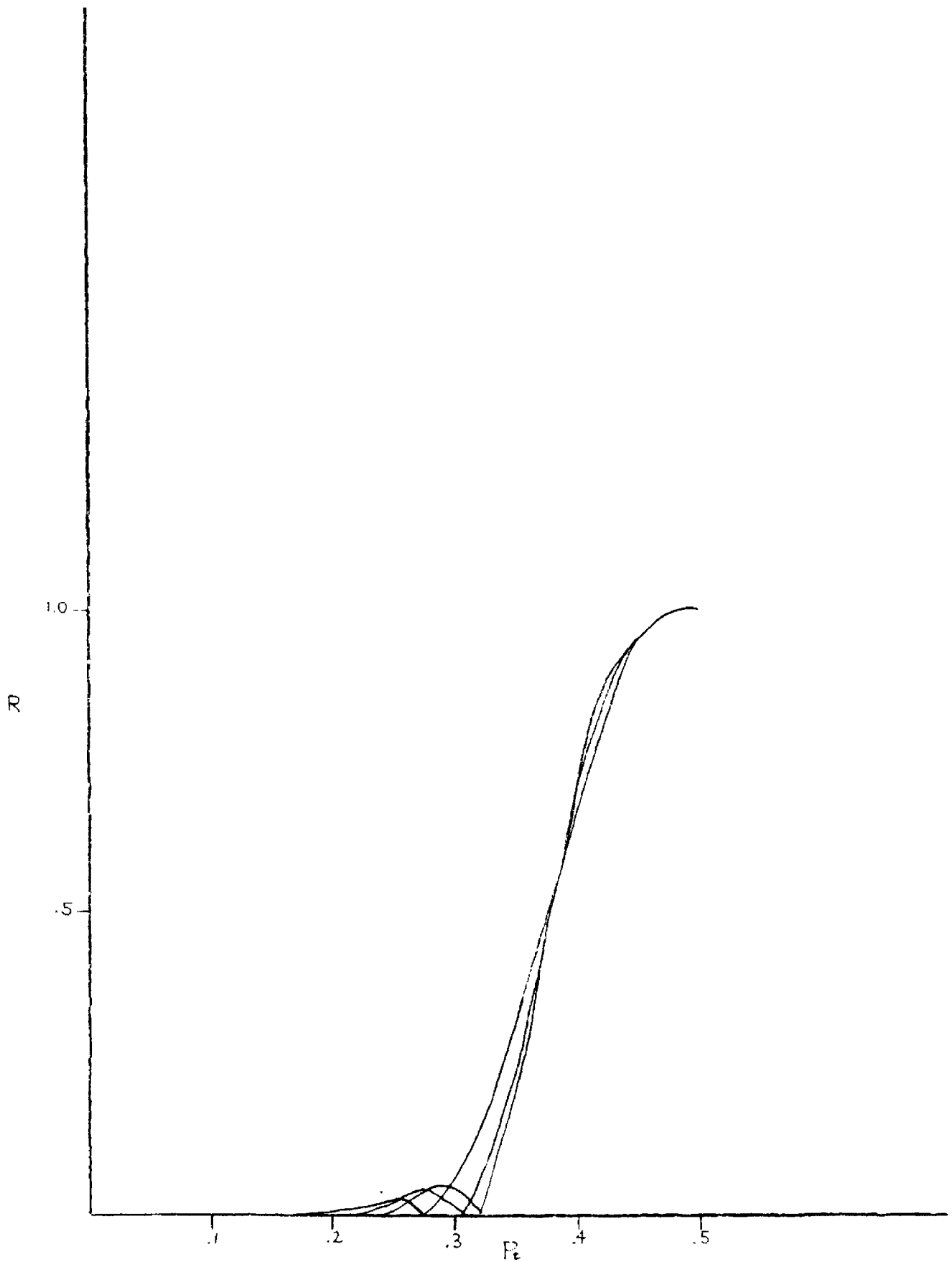


Figure 3.11
Order Parameter Vs. Density Fixed Boundary

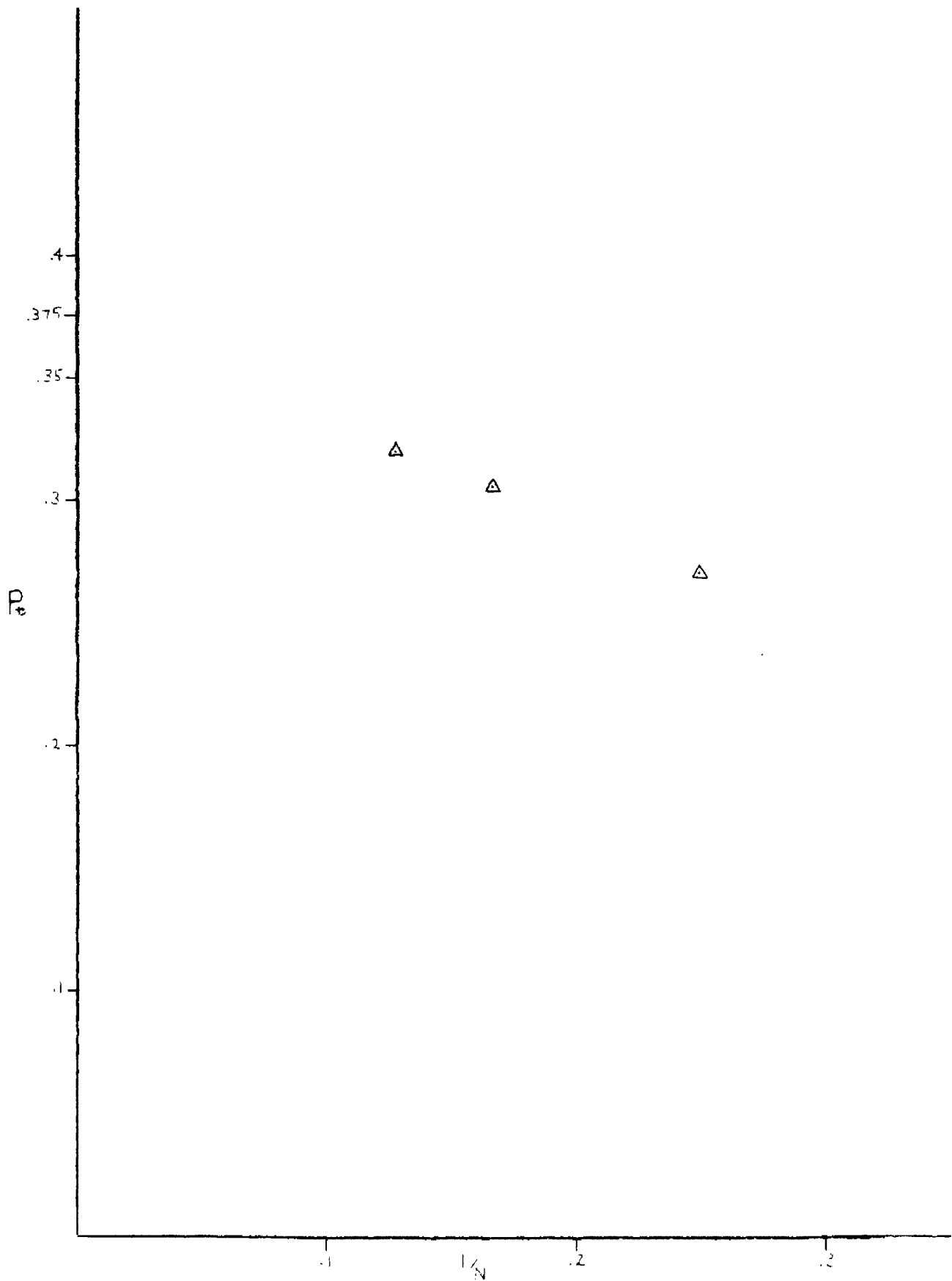


Figure 3.12
Order Parameter Minimum Vs. $1/n$ Fixed Boundary

give a transition density very near the "exact" result ($P_{tr} = 0.370$). Figure 3.13 is a pressure versus density isotherm. Again we see an excellent convergence to the "exact" result tabulated by Ree and Chestnut. Compressibility for the fixed boundary system is shown in figure 3.14 and specific heat in figure 3.15. Figure 3.16 is a plot of the specific heat maximum versus the logarithm of N . Here again we see an asymptotic linear relation which indicates an infinite specific heat maximum. In general, we observe that the fixed boundary system converges more rapidly to the exact results than does the free boundary system enhancing its value as an approximation technique.

A surface tension was also calculated using the fixed boundary technique. This surface tension was calculated using both equations 2.48 and 2.49, whose results in turn were used in equation 2.50. The results of the surface tension calculations are shown in figures 3.17 and 3.18. Equation 2.48 was used to obtain figure 3.17 and equation 2.49 for figure 3.18. The surface tension appears to be an excellent indicator of the position of the phase transition as we observe a rapid increase in the surface tension as we approach the region of phase transition. The surface tension was calculated for the 2 - 4, and 4 - 6 systems only so that it would be meaningless to plot the point of appearance of the surface tension versus the size of the system, however, if more data were available, such a plot would be very useful. These surface tension results are quite similar to those calculated by Woodbury using a modified EFM procedure. Surface

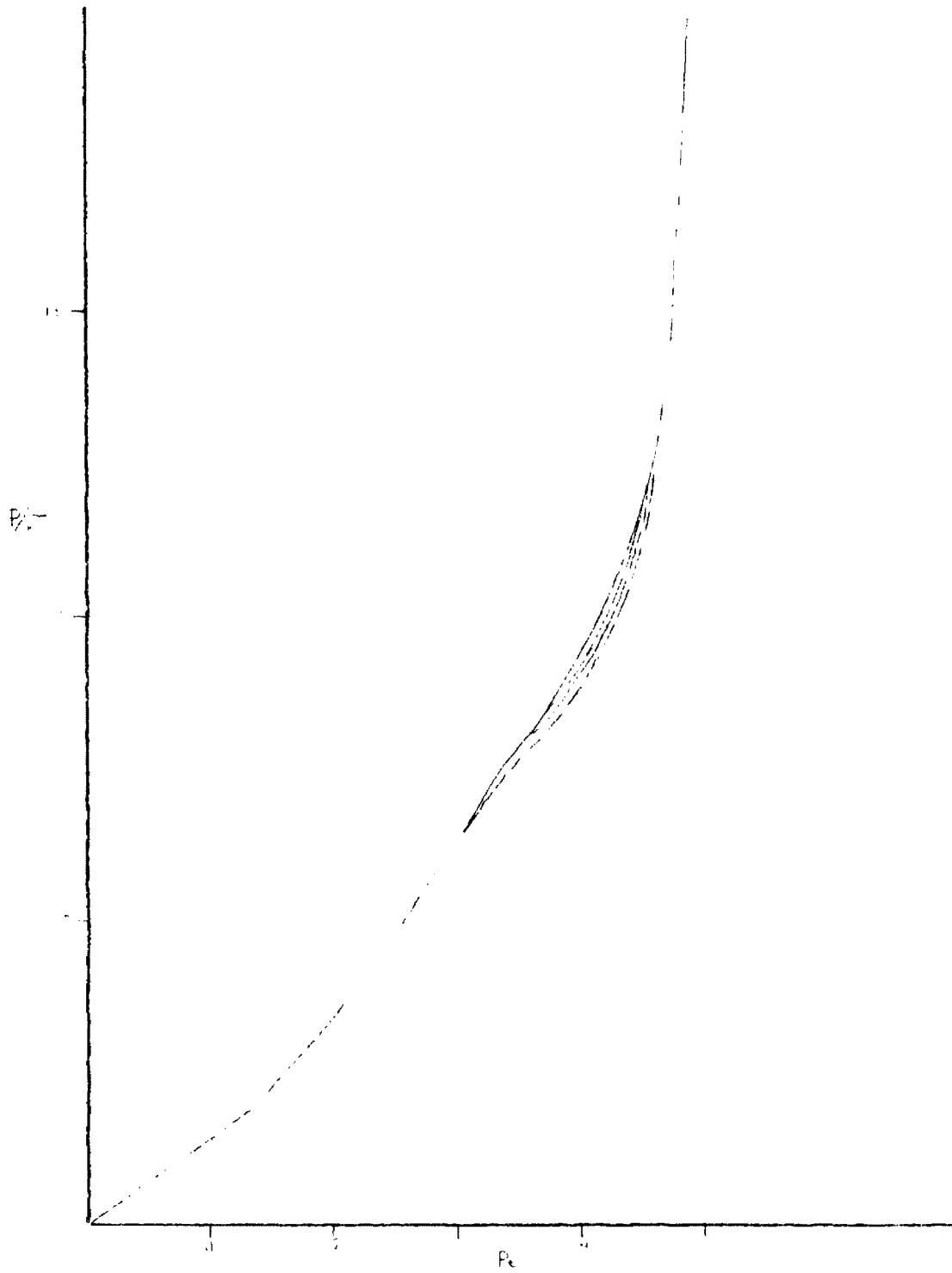


Figure 3.13
Pressure Vs. Density Fixed Boundary

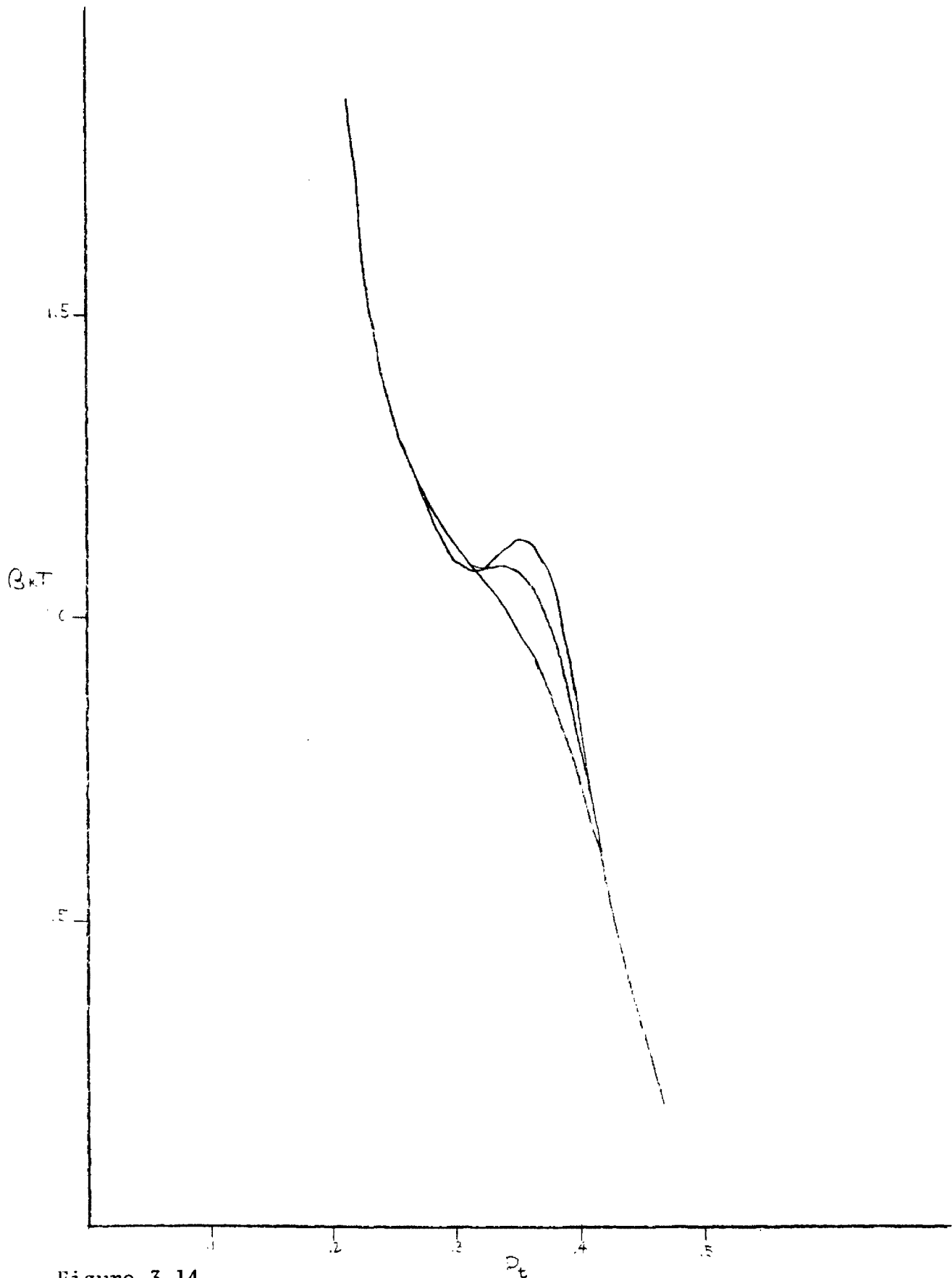


Figure 3.14
Compressibility Vs. Density Fixed Boundary

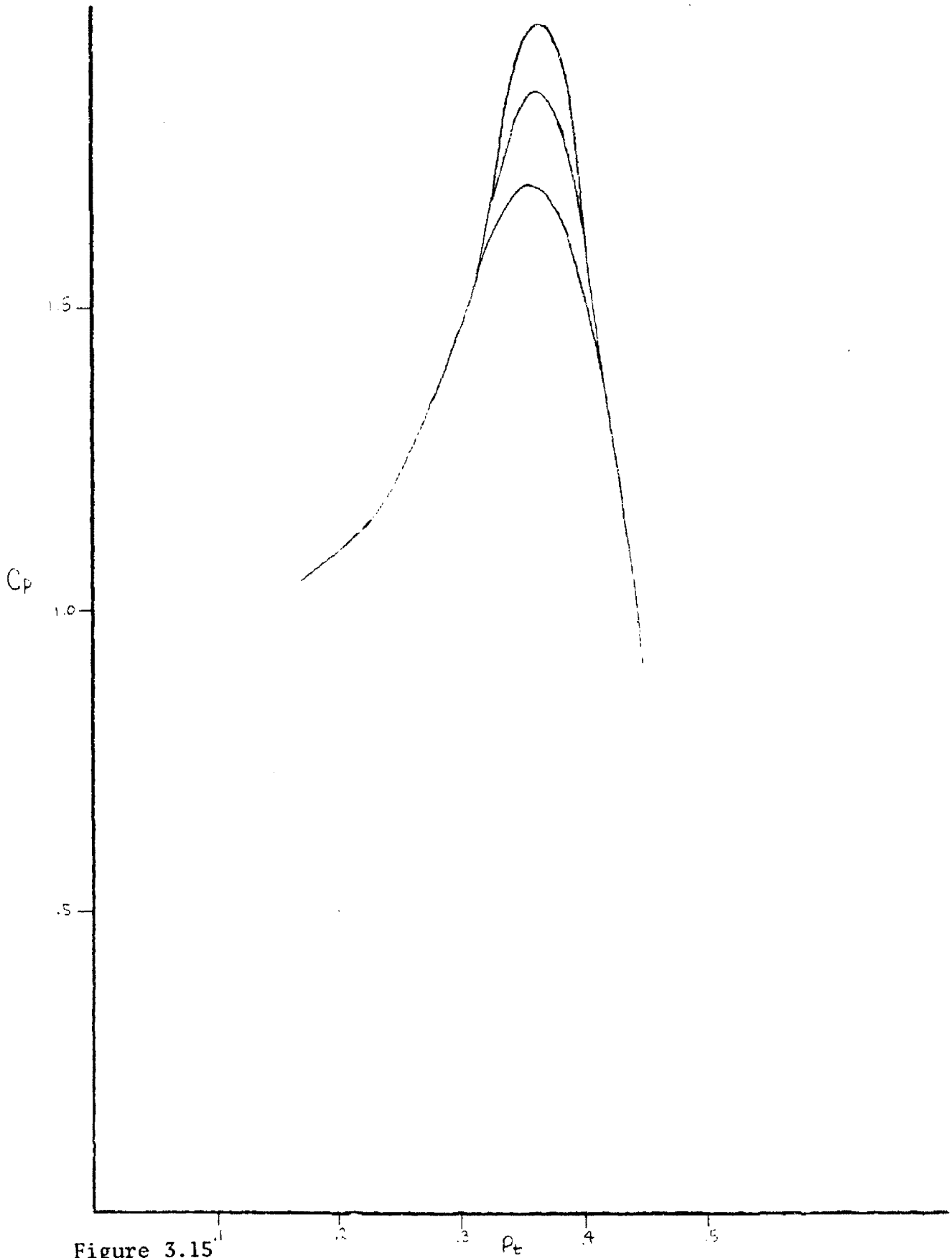


Figure 3.15
Heat Capacity Vs. Density Fixed Boundaries

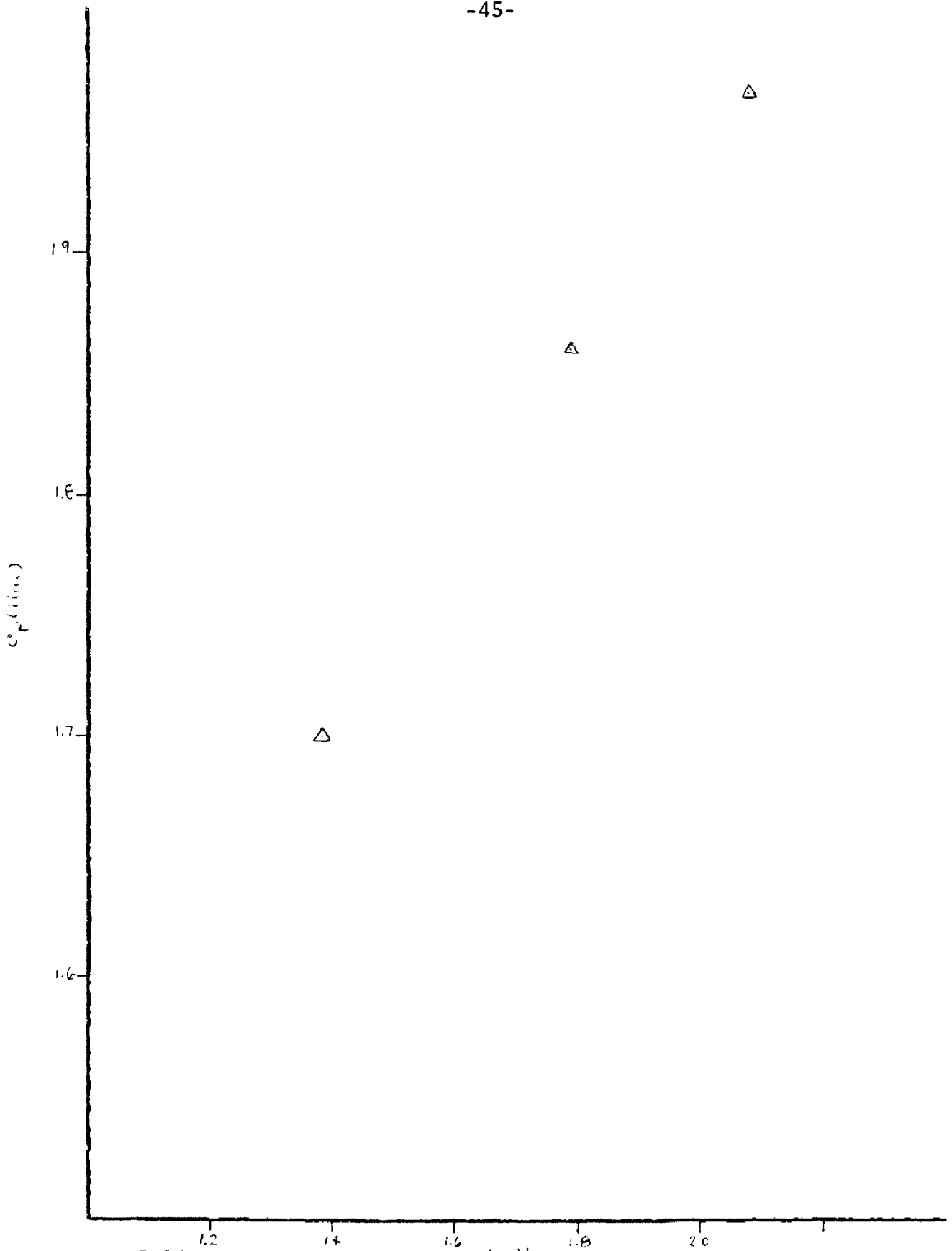


Figure 3.16
Heat Capacity Maximum Vs. Log N Fixed Boundary System

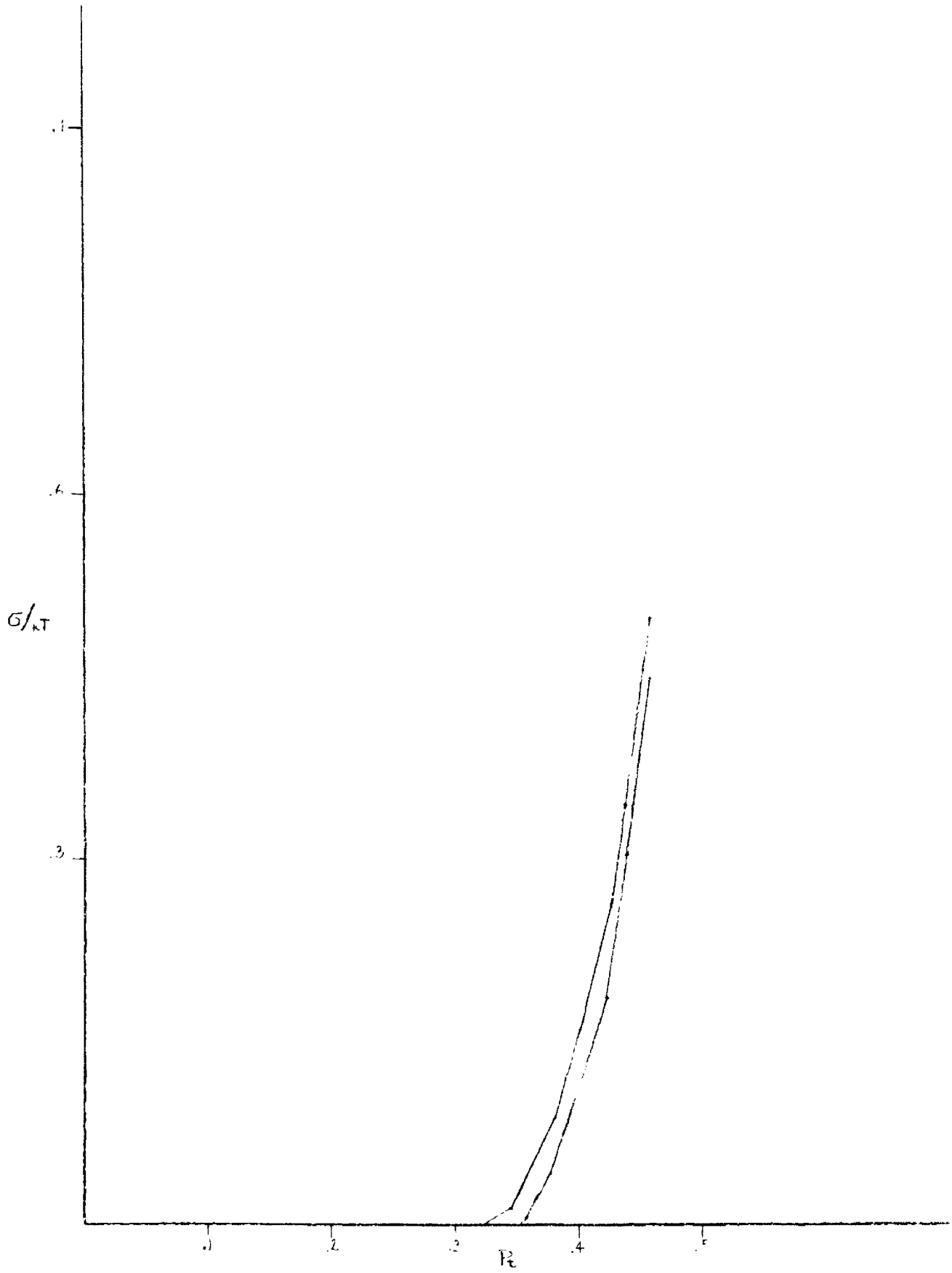


Figure 3.17
Method 1 Surface Tension 2xn-4xn, 4xn-6xn

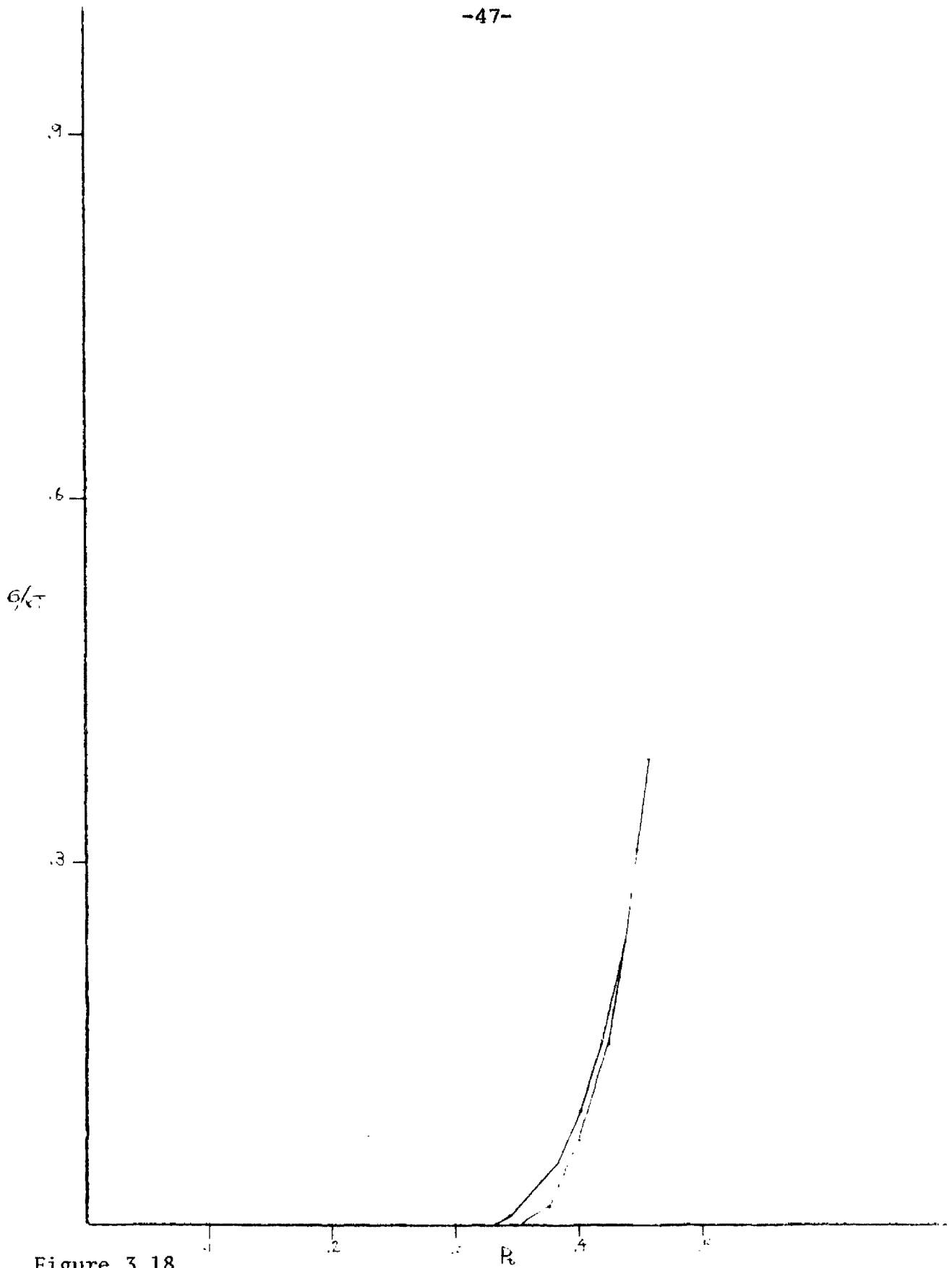


Figure 3.18
Method 2 Surface Tension $2x_n-4x_n, 4x_n-6x_n$

tension calculations have only recently been applied to lattice gas models: however, the results obtained thus far are gratifying and certainly justify continued study.

Chapter 4

SUMMARY AND CONCLUSIONS

The TSM appears to be a useful approximation technique for lattice statistics. The approximation certainly appears to yield excellent results with the hard square lattice gas. The TSM yields all of the thermodynamic information presented by the various authors in their "exact" calculations; in addition a surface tension and an order parameter can also be calculated. Gaunt and Fisher's calculation is the only other "exact" result which has statistical information in a form useful for an order parameter calculation, and no previous method provides the information for the surface tension calculation. The rapid convergence of the TSM and the small size of the systems involved is appealing in calculations which are computer limited. These same features are also economically appealing, of course.

Thus far the TSM has been applied only to the hard square lattice gas; however, this method is certainly not restricted to one particular lattice model. The TSM is hopefully a method of general utility. The hard sphere lattice gas with other than nearest neighbor exclusions is an interesting problem and one that is just beginning to be explored. It is hoped that by increasing the number of lattice sites excluded, the properties of the hard disc continuum

fluid can be approached. The TSM is certainly adaptable to this problem, and this is an area of possible future research.

Appendix 1
TSM COMPUTER PROGRAM

This appendix contains the actual programs used in the TSM calculation. Although many preliminary calculations were performed on an IBM 1620 computer at the University of Montana, all of the calculations included in this thesis were computed on an SDS Sigma 7 computer at Montana State University because of storage and time requirements. A remote time share terminal for the Sigma 7 was used with very satisfactory results. All of the programs used were coded in Fortran IV.

Program 1 is the standard TSM calculation. Output from this program includes the density, sublattice densities, order parameter, pressure, compressibility, and heat capacity for each input z value. Input data includes information about the size of the systems and the desired activity, z , values. Program one was later modified to calculate a surface tension. The only information necessary for a surface tension calculation is statistical information about sublattices A and B which was readily available. Program 2 contains the modifications necessary for a surface tension calculation. The only output from program 2 is the surface tension for each input activity value. Input data for program 2 was the same as for program 1. Teletype output was used for both of these programs as only a low speed paper tape punch was available.

Program 1

```
1.000      READ 100, MX, N, K, KX
2.000      DIMENSION ANT(50,8), BNT(50,8),EV950)
3.000      DIMENSION AX(6,21),C(21)
4.000      DIMENSION A(21,21),B(21),P(21),ANORM(21),Z(50)
5.000      DIMENSION FMT(18), SFMT(18), TFMT(18)
6.000      READ 101,FMT
7.000      READ FMT, ((AX(I,J),I=1,MX),J=1,N)
8.000      NX=N-1
9.000      NKX=1
10.000     DO 20 J=1,NX
11.000     DO 21 M=NKX,NX
12.000     ZOOM=0.
13.000     DO 25 I=1,MX
14.000     CX=AX(I,J)+AX(I,M+1)
15.000     IF (CX.CT.1.) GO TO 35
16.000     ZOOM = ZOOM + CX
17.000     GO TO 25
18.000  35  ZOOM = 1000.
19.000  25  CONTINUE
20.000     IF (ZOOM.GE.1000.) GO TO 27
21.000     A(J,M+1) = ZOOM*.5
22.000     A(M+1,J) = ZOOM*.5
23.000     A(J,J) = 10.
24.000     GO TO 21
25.000  27  A(J,M + 1) = 10.
26.000     A(M + 1, J) = 10.
27.000     A(J,J) = 10.
28.000  21  CONTINUE
29.000     NKX = NKX + 1
30.000  20  CONTINUE
31.000     A(L,L) = 1.
32.000     A(N,N) = 10.
33.000     READ 101, SFMT
34.000     READ SFMT, (B(J), J = 1, N)
35.000     READ 101, TFMT
36.000     READ TFMT,(Z(I),( = 1,K)
37.000     NOREP = 0
38.000     ABBB = 0
39.000     K = 1
40.000     DO 46 J = 1,N
41.000  46  C(J) = B (J)
42.000  125 DO 50 J = 1,N
43.000  50  B(J) = Z(K)**B(J)
44.000     DO 55 I = 1,N
45.000     DO 55 J = 1,N
46.000     IF (A(I,J).GE.10.) GO TO 65
47.000     A(I,J) = Z(K)**A(I,J)
48.000     GO TO 55
49.000  65  A(I,J) = 0.
50.000  55  CONTINUE
```

Program 1

```
51.000      A(1,1) = 1.
52.000  70    DO 75 I = 1,N
53.000      P(I) = 0.
54.000      DO 75 J = 1,N
55.000  75    P(I) = P(I) +A(I,J)*B(J)
56.000      DO 80 I = 1,N
57.000  80    ANORM(I) = P(I)**2
58.000      DO 85 I = 1,N
59.000      AAA = ANORM(I)
60.000      CNORM = AAA + ABBB
61.000  85    ABBB = ABBB + ANORM(I)
62.000      BNORM = 1./SQRT(CNORM)
63.000      DO 90 I = 1,N
64.000  90    B (I) = P(I)*BNORM
65.000      NOREP = NOREP + 1
66.000      IF (NOREP.GE.KX) GO TO 105
67.000  95    ABBB = 0.
68.000      GO TO 70
69.000  105   LT = KX +1
70.000      IF (NOREP.GE.LT) GO TO 110
71.000      DO 106 I = 1,N
72.000  106   ANT (K,I) = B(I)
73.000      GO TO 95
74.000      DO 107 I =1,N
75.000  107   BNT(K,I) = B(I)
76.000      EV(K) = BNORM
77.000      ABBB = 0.
78.000      NOREP = 0
79.000      DO 115 I = 1,N
80.000      DO 115 J = 1,N
81.000      IF (A(I,J).EQ.0.) GO TO 117
82.000      A(I,J) = ALOG (A(I,J))/ALOG(Z(K))
83.000      GO TO 115
84.000  117   A(I,J) = 10.
85.000  115   CONTINUE
86.000      DO 120 J = 1,N
87.000  120   B(J) = C(J)
88.000      K = K + 1
89.000      IF (Z(K).NE.500.) GO TO 125
90.000  100   FORMAT (415)
91.000  101   FORMAT (18A4)
92.000  102   FORMAT (2HZ =, F10.6)
93.000      READ 100, MX,N,K,KX
94.000      DIMENSION CNT(50,21),DNT(50,21), SEV(21)
95.000      READ 101,FMT
96.000      READ FMT, ((AX(I,J),I = 1,MX), J = 1,N)
97.000      NX = N,1
98.000      NKX = 1
99.000      DO 320 J = 1, NX
100.000     DO 321 M = NKX,NX
```

Program 1

```
101.000      ZOOM = 0.
102.000      DO 325 I = 1,MX
103.000      CX=AX(I,J) + AX(I,M + 1)
104.000      IF (CX.GT.1.) GO TO 335
105.000      ZOOM = ZOOM + CX
106.000      GO TO 325
107.000 335   ZOOM = 1000.
108.000 325   CONTINUE
109.000      IF (ZOOM.GE.1000.) GO TO 327
110.000      A(J,M + 1) = ZOOM*.5
111.000      A(M + 1,J) = ZOOM* .5
112.000      A (J,J) = 10.
113.000      GO TO 321
114.000 327   A (J,M + 1) = 10.
115.000      A (M + 1,J) = 10.
116.000      A(J,J) = 10.
117.000 321   CONTINUE
118.000      NKX = NKX + 1
119.000 320   CONTINUE
120.000      A (1,1) = 1.
121.000      A (N,N) = 10.
122.000      READ 101, SFMT
123.000      READ SFMT, (B(J), J = 1,N)
124.000      NOREP = 0
125.000      ABBB = 0.
126.000      K = 1
127.000      DO 346 J = 1,N
128.000 346   C(J) = B(J)
129.000 425   DO 350 J = 1,N
130.000 350   B(J) = Z(K)**B(J)
131.000      DO 355 I = 1,N
132.000      DO 355 J = 1,N
133.000      IF (A(I,J).GE.10.) GO TO 365
134.000      A(I,J) = Z(K)**A(I,J)
135.000      GO TO 355
136.000 365   A(I,J) = 0.
137.000 355   CONTINUE
138.000      A(I,1) = 1.
139.000 370   DO 375 I = 1,N
140.000      P (I) = 0.
141.000      DO 375 J = 1,N
142.000 375   P(I) = P(I) + A(I,J)*B(J)
143.000      DO 380 I = 1,N
144.000 380   ANORM (I) = P(I)**2
145.000      DO 385 I = 1,N
146.000      AAA = ANORM (I)
147.000      CNORM = AAA + ABBB
148.000 385   ABBB = ABBB + ANORM (I)
149.000      BNORM = 1./SQRT (CNORM)
150.000      DO 390 I = 1,N
```

Program 1

```
151.000 390      B(I) = P(I)*BNORM
152.000      NOREP = NOREP + 1
153.000      IF (NOREP.GE.KX) GO TO 405
154.000 395      ABBB = 0.
155.000      GO TO 370
156.000 405      LT = KX + 1
157.000      IF (NOREP.GE.LT) GO TO 410
158.000      DO 406 I = 1,N
159.000      CNT (K,I) = B(I)
160.000      GO TO 395
161.000 410      DO 407 I = 1,N
162.000 407      DNT (K,I) = B(I)
163.000      SEV (K) = BNORM
164.000      ABBB = 0.
165.000      NOREP = 0
166.000      DO 415 I = 1,N
167.000      DO 415 J = 1,N
168.000      IF (A(I,J).EQ.0.) GO TO 417
169.000      A (I,J) = ALOG (A(I,J))/ALOG (Z(K))
170.000      GO TO 415
171.000 417      A (I,J) = 10.
172.000 415      CONTINUE
173.000      DO 420 J = 1,N
174.000 420      B(J) = C(J)
175.000      K = K + 1
176.000      IF (Z(K).NE.500.) GO TO 425
177.000      DIMENSION E(8), E2(8), F(21), F2 (21)
178.000      DIMENSION XMT (18), FFMT (18)
179.000      DIMENSION RHO (50), PKT (50)
180.000      READ 500, LK,SNT
181.000      DO 507 I = 1,K
182.000      DO 507 J = 1,LK
183.000 507      ANT (I,J) = ANT (I,J)*ANT (I,J)
184.000      DO 508 I = 1,K
185.000      DO 508 J = 1,LK
186.000 508      ENT (I,J) = BNT (I,J)*BNT(I,J)
187.000      DO 509 I = 1,K
188.000      DO 509 J = 1,N
189.000 509      CNT (I,J) = CNT (I,J)*CNT (I,J)
190.000      DO 512 I = 1,K
191.000      DO 512 J = 1,N
192.000 512      DNT (I,J) = DNT (I,J)* DNT (I,J)
193.000      READ 101, XMT
194.000      READ XMT, (E(J), J = 1, LK), (E2(J), J = 1, LK)
195.000      READ 101, FFMT
196.000      READ FFMT, (F(J), J = 1,N), (F2(J),J = 1, N)
197.000      I = 1
198.000 513      FLIP = 0.
199.000      FLAP = 0.
200.000      ZIP = 0.
```

Program 1

```
201.000      ZAP = 0.
202.000      DO 520 J = 1,LK
203.000      ZIP = ZIP + ANT (I,J) *E(J)
204.000      ZAP = ZAP + ANT (I,J)*E2(J)
205.000      FLIP = FLIP + BNT (I,J)*E(J)
206.000 520   FLAP = FLAP + BNT (I,J)*E2(J)
207.000      SFLIP = 0.
208.000      SFLAP = 0.
209.000      SZIP = 0.
210.000      SZAP = 0.
211.000      DO 525 J = 1,N
212.000      SZIP = SZIP + CNT (I,J)*F(J)
213.000      SZAP = SZAP + CNT (I,J)*F2(J)
214.000      SFLIP = SFLIP + DNT (I,J)*F(J)
215.000 525   SFLAP = SFLAP + DNT (I,J,)*F2(J)
216.000      RHOA = (SNT*(SZIP + SFLAP)-((SNT-1.)*(ZIP + FLAP)))/2.
217.000      RHOB = (SNT*(SZAP+SFLIP)-((SNT-1.)*(ZAP+FLIP)))/2.
218.000      RHO(I) = RHOA + RHOB
219.000      IF (RHOA.LE.RHOB) GO TO 526
220.000      ORD = 2.*(RHOB - RHOA)
221.000      GO TO 527
222.000 526   ORD = 2.* (RHOB - RHOA)
223.000 527   RED = 1./EV(I)
224.000      WHITE = 1./SEV(I)
225.000      PKT (I) =.5*(ALOG(WHITE)-ALOG((RED)))
226.000      PRINT 102,Z(I)
227.000      PRINT 502, RHOA,RHOB,RHO(I)
228.000      PRINT 503,ORD
229.000      I = I + 1
230.000      IF (I.LE.K) GO TO 513
231.000 500   FORMAT (15,F10.5)
232.000 502   FORMAT (F10.6,2X,F10.6,2X,4HDEN=,F10.6)
233.000 503   FORMAT (16HORDER PARAMETER=,F10.8)
234.000 504   FORMAT (5HP/KT=,F10.6)
235.000      READ 600,H
236.000      NIX=K-5
237.000      DO 625 I=1,NIX
238.000      DRHO=(-.25*RHO(I+4)+1.33333333*RHO(I+3)-3.*RHO(I+2)
239.000      1 + 4.*RHO(I+1)-2.08333333*RHO(I)))/H
240.000      ZOOM = 1./(RHO(I)*RHO(I))
241.000      ROOM=1./(RHO(I)*RHO(I)*RHO(I))
242.000      WHAM=PKT(I)*PKT(I)
243.000      COMP=ZOOM*Z(I)*DRHO
244.000      HCAP=ROOM*WHAM*Z(I)*DRHO
245.000      PRINT 102, Z(I)
246.000      PRINT 605, RHO(I)
247.000      PRINT 504, PKT(I)
248.000      PRINT 603, COMP
249.000      PRINT 604, HCAP
250.000 625   CONTINUE
```

Program 1

```
251.000 600      FORMAT (F10.5)
252.000 603      FORMAT (16HCOMPRESSIBILITY=,F10.5)
253.000 604      FORMAT (14HHEAT CAPACITY=,F10.5)
254.000 605      FORMAT (4HDEN=,F10.6)
255.000          STOP
256.000          END
*
```

Program 2

```
173.000      IO 420 J=1,N
174.000  420      B(J)=C(J)
175.000      K=k+1
176.000      IF (Z(K).NE.500.) GO TO 425
177.000      DIMENSION E(8),E2(8),F(21),F2(21)
178.000      DIMENSION XMT(18),FFMT(18)
179.000      DIMENSION RHO(50),PKT(50)
180.000      READ 500,LK,SNT
181.000      DO 507 I =1,K
182.000      DO 507 J=1,LK
183.000  507      ANT(I,J)=ANT(I,J)*ANT(I,J)
184.000      DO 508 I=1,K
185.000      DO 508 J-1,LK
186.000  508      BNT(I,J)=BNT(I,J)*BNT(I,J)
187.000      DO 509 I=1,K
188.000      DO 509 J=1,N
189.000  509      CNT(I,J)=CNT(I,J)*CNT(I,J)
190.000      DO 512 I=1,K
191.000      DO 512 J=1,N
192.000  512      DNT(I,J)=DNT(I,J)*DNT(I,J)
193.000      READ 101,XMT
194.000      READ XMT, (E(J),J=1,LK),(E2(J),J=1,LK)
195.000      READ 101, FFMT
196.000      READ FFMT, (F(J),J=1,N),(F2(J),J=1,N)
197.000      I=1
198.000  513      ZIP=0.
199.000      DO 520 J=1,LK
200.000  520      ZIP=ZIP+(ANT(I,J)-BNT(I,J))*ALOG(ANT(I,J))
*TY 200-300
200.000  520      ZIP=ZIP+(ANT(I,J)-BNT(I,J))*ALOG(ANT(I,J))
201.000      AMX=MX
202.000      SUR=ZIP/(2.*(AMX-2.))
203.000      ZAP=0.
204.000      DO 521 J=1,LK
205.000  520      ZAP=ZAP+SORT(ANT(I,J))*SQRT(BNT(I,J))
206.000      SURF=ALOG(ZAP)/(AMX-2.)
207.000      FLIP=0.
208.000      DO 522 J=1,N
209.000  522      FLIP=FLIP+(CNT(I,J)-DNT(I,J))*ALOG(CNT(I,J))
210.000      SUR1=FLIP/(2.*AMX)
211.000      FLAP=0.
212.000      DO 523 J=1,N
213.000  523      FLAP=FLAP+SQRT(CNT(I,J))*SQRT(DNT(I,J))
214.000      SURF1=ALOG(FLAP)/AMX
215.000      STI=SNT*SUR1-(SNT-1.)*SUR
216.000      ST2=SNT*SURF1-(SNT-1.)*SURF
217.000      PRINT 102, Z(I)
218.000      PRINT 502, ST1,ST2
219.000      I=I+1
220.000      IF(I.LE.K) GO TO 513
*** 500  500      FORMAT (15,F10.5)
                FORMAT (F10.6,4X,F10.6)
                STOP
                END
```


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