ASYMPTOTIC BEHAVIOR OF PAIR CORRELATIONS IN ONE-DIMENSIONAL BINARY MIXTURES

by

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ABSTRACT

The asymptotic behavior of the pair correlation functions of a one-dimensional binary mixture of simple model fluids is investigated. The method of investigation is an extension of a technique developed by Fisher and Widom[1] for simple one-component systems. The technique consists of examining the poles of the Laplace transform of the pair correlation function to determine the pole of least negative real part. The present investigation has been restricted to systems interacting through either hard-sphere or square-well intermolecular pair potentials. In all cases the pair potentials are short ranged and strictly nearest-neighbor.

The actual extraction of the poles of the Laplace transform of the pair correlation functions is carried out numerically. One specific case of a hard-sphere system has been solved analytically. In the case of hard spheres, a locus is generated in the density, concentration plane across which, the pair correlation function abruptly changes its spatial frequency. Both linear continum and lattice gas models are investigated for the hard-sphere systems and the results are found to be in qualitative agreement with each other.

The square-well systems exhibit loci which divide the density temperature plane into several regions. Each region is characterized by the value of the spatial frequency associated with the damped sinusodial

decay of the pair correlation function. The zero frequency region corresponds to monotonic exponential decay.

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INTRODUCTION

Much of physics deals with systems of enormously many degrees of freedom. The investigation of such systems is greatly facilitated if attention can be restricted to quantities of direct physical significance. While there is little difficulty in selecting a few physical parameters which encompass all information which can reasonably be required, it is far more difficult to formulate a theory, even an approximate one, which relates these few physically significant quantities to the almost infinite number of degrees of freedom of the system. For a classical fluid in thermal equilibrium, the pair correlation function provides the necessary link between the interparticle forces and the bulk of single-time observations which can be made.

The mean local density $\rho(r)$ at a distance r from any given particle in the system differs from the overall average density ρ_o. The radial distribution function g(r) is defined as the ratio of these two densities, and the pair correlation G(r) as g(r)-1. Hence

$$G(r) = (\rho(r)/\rho_o) - 1 \quad . \tag{A}$$

With this definition the pair correlation function is then a measure of the degree of correlation, or structure, that exists around the chosen particle.

The pair correlation function is related to the thermodynamic properties of the system through various relations. For example, the fluctuation compressibility theorem

$$kT \frac{\partial \rho}{\partial p}_T = kT\rho \, k_T = 1 \quad \rho \int G(r)dr \quad , \qquad \text{(B)}$$

where ρ is the number density, p is the pressure, T is the absolute temperature, k_T is the isothermal compressibility, and k is Boltzmann's constant. (Occasionally Boltzmann's constant will be represented by k_B).

Since we are interested in the long range properties of the correlation function, we want to know how G(r) behaves for large values of r. We already know that $G(r) \rightarrow 0$, as $r \rightarrow \infty$ since, as stated before, there is no gross overall structure to our liquid models. However, we wish to know how this approach to zero takes place. To this end we shall follow the methods of Fisher and Widom[1] and examine the Laplace transform of the pair correlation function. The poles of the transform will give us information concerning the asymptotic behavior of G(r).

Previous work[1,2,3] has shown that if the correlation at long range reflects primarily the correlating effects of the intermolecular repulsions, then the decay of the correlation function is expected to be oscillatory, whereas if it reflects the correlating effects of the attractive component of the intermolecular potential, then G(r) will be asymptotically positive and its decay monotonic.

Thus in a system with an intermolecular potential that contains both attractive and repulsive components one might expect regions in the thermodynamic state space of the system where the asymptotic decay of $G(r)$ is either oscillatory or monotonic depending upon the particular thermodynamic state of the system. Indeed, such regions have been found for several types of intermolecular pair potentials.[1,3]

For the present study we shall be interested in binary mixtures of simple model fluids. All our systems will be described by an intermolecular pair potential $\phi_{ij}(r)$ which is bounded below, has an infinite repulsion as $r \rightarrow 0$, and is strictly nearest neighbor, i.e. particle i interacts only with particles i-1 and i + 1. For these binary mixtures the mixed interaction parameters of the pair potential will be given by the Lorentz-Berthelot[4] combining rules

$$b_{12} = (b_1 + b_2)/2 \tag{C}$$

and

$$\epsilon_{12} = (\epsilon_1 \epsilon_2)^{1/2} , \tag{D}$$

where b_i is the hard-core diameter of an i type particle and ϵ_i is the well depth. Equation (C) is, of course, exact for a mixture of hard spheres. Our two mixing parameters are N, the ratio of the hard-core diameter of the larger species to the hard-core diameter of the smaller species, and H, the ratio of the well-depth of the larger species to the well-depth of the smaller species. Thus

$$N = b_{22}/b_{11} \quad , \tag{E}$$

and

$$H = \epsilon_{22}/\epsilon_{11} \quad , \tag{F}$$

where the subscript (11) refers to the smaller species. The values chosen for N were somewhat larger than what one would find for real systems. This was done to emphasize the effect of the hard-core repulsions. The values of H were close to those found in real systems.[5] One additional parameter R, the ratio of the well-depth to the hard-core diameter for a single species, was included. In the present work R was always set equal to one for both species.

When we examine the asymptotic behavior of G(r) we find that it can have various forms depending upon the thermodynamic state of the system. Thus we generate loci in the (p, T), (ρ, T), and (T, x_1) planes across which the asymptotic decay of the pair correlation function abruptly changes. Here x_1 is the concentration of the smaller species. The transition loci divide the state space of the system into several regions. Each region is characterized by the value of the spatial frequency associated with the damped sinusoidal decay of G(r). The zero frequency region corresponds to monotonic exponential decay.

The first part of the thesis is concerned with deriving the equations for the pole of least negative real part of the Laplace transform of the pair correlation function. Once these equations and the equation of state are derived they are applied to hard-sphere and square-well linear continuum systems. The next section carries out the calculation for a hard-sphere lattice gas. The final section is devoted to evaluation of the results obtained from the calculations.

We note here that these abrupt changes in the asymptotic form of the pair correlation function in no way imply a phase transition in our our-dimensional systems. Indeed, the systems treated are completely without any phase transition.

DERIVATION OF BASIC EQUATION

Consider a one-dimensional system of N_1 particles of type 1 and N_2 particles of type 2, where $N_1 + N_2 = M$. Let the particles interact on a line of length L through a strictly nearest-neighbor pair potential $\emptyset_{ij}(r)$. We shall be interested in the thermodynamic limit of this system, i.e. $L \to \infty$, $M \to \infty$, $M/L \to \rho$ and $N_1/M \to x_1$.

Following Lebowitz and Zomick[6] we define the conditional probability $P_{ij}^{(n)}(r)$ such that

$P_{ij}^{(n)}(r)$ = conditional probability density that the nth neighbor of a given particle of species i is a particle of species j located a distance r away. (1.1)

Then

$$P_{ij}^{(n)}(r) = \sum_{k=1}^{2} \int_o^r P_{ik}^{(n-1)}(r')P_{kj}^{(1)}(r-r')dr' \quad . \tag{1.2}$$

The radial distribution function $g_{ij}(r)$ is then given by

$$\rho_j g_{ij}(r) = \sum_{n=1}^{\infty} P_{ij}^{(n)}(r) \quad . \tag{1.3}$$

Hence, defining the symmetric Laplace transforms

$$G_{ij}(\sigma) = \int_o^{\infty} e^{-\sigma r} (\rho_i \rho_j)^{1/2} g_{ij}(r)\, dr \quad , \tag{1.4}$$

and

$$P_{ij}(\sigma) = \int_o^{\infty} e^{-\sigma r} (\rho_i/\rho_j) P_{ij}^{(1)}(r)\, dr \quad . \tag{1.5}$$

we have, in matrix notation

$$\underline{G}(\sigma) = \underline{P}(\sigma)\,(\underline{I} - \underline{P}(\sigma))^{-1} \quad , \tag{1.6}$$

where $\underline{I}$ is the unit matrix.

Equation (1.6) will be the basic equation for our analysis. The pole of $\underline{G}(\sigma)$ at $\sigma = 0$ will contribute a constant to $g_{ij(r)}$. Hence, the asymptotic form of $G_{ij}(r)$ will then be determined by the nature of the singularity (possibly more complex than a pole) of next largest real part.[1] Thus

$$G(r) \sim \gamma_1 e^{\sigma_1 r} \quad , \tag{1.7}$$

where γ_1 is the residue at the pole of least negative real part σ_1. If σ_1 is real, G(r) will decay monotonically from positive values. If σ_1 is complex, G(r) will decay as a damped sinusoid. Let the inverse range of correlation k be given by $\kappa = -\mathrm{Re}(\sigma_1)$ and the spatial frequency ω by $\omega = \mathrm{Im}(\sigma_1)$, then

$$G(r) \sim \gamma_1 e^{-\kappa r}, \quad \sigma_1 \text{ real} \tag{1.8}$$

and

$$G(r) \sim 2|\gamma_1|\, e^{-\kappa r} \cos(\omega r + \arg(\gamma_1)), \quad \sigma_1 \text{ complex} \quad . \tag{1.9}$$

Now let

$$\underline{I} - \underline{P}(\sigma) = \underline{D}(\sigma) \quad . \tag{1.10}$$

Then

$$\underline{G}(\sigma) = \underline{P}(\sigma)\, \underline{D}^{-1}(\sigma) \quad , \tag{1.11}$$

with

$$(\underline{D}^{-1}(\sigma))_{ij} = \frac{D'_{ij}(\sigma)}{|\underline{D}(\sigma)|} \quad , \tag{1.12}$$

$$= \frac{D_{ji}(\sigma)}{|D(\sigma)|} \quad ,$$

where $D_{ij}(\sigma)$ is the cofactor of the (ij)th element of $\underline{D}(\sigma)$ and $|\underline{D}(\sigma)|$ is the determinant of $\underline{D}(\sigma)$. Writing out equation (1.11) in component form

$$G_{ij}(\sigma) = \sum_{k=1}^{2} P_{ik}(\sigma) \, (\underline{D}^{-1}(\sigma))_{kj} \tag{1.13}$$

$$= \sum_{k=1}^{2} P_{ik}(\sigma) \, D_{jk}(\sigma) / \, \underline{D}(\sigma) \quad .$$

Thus the asymptotic form of $G_{ij}(r)$ will be determined from

$$|\underline{D}(\sigma)| = 0 \quad , \tag{1.14}$$

or

$$1 - P_{11} - P_{22} + P_{11}P_{22} - P_{21}P_{12} = 0 \quad . \tag{1.15}$$

We now wish to derive expressions for the $P_{ij}(\sigma)$'s. First we note the following theorem from probability theory.[7] Let

$P(A)$ = probability of A ,

$P(AB)$ = probability of A and B ,

and $P_A(B)$ = probability of B given A ,

then

$$P_A(B) = P(AB)/P(A) \quad . \tag{1.16}$$

Using a method due to Kikuchi,[8] we define a two-point probability density function $f_{ij}(\gamma_i, \gamma_j')$ such that

$f_{ij}(\gamma_i, \gamma_j')$ = probability density that the first neighbor of a particle of species i located at γ_i is a particle of species j located at γ_j'.

Then substituting (1.1) and (1.17) into equation (1.16) we have

$$P_{ij}^{(1)}(r) = (L/x_i)f_{ij}(\gamma_i, \gamma_j') \qquad , \tag{1.18}$$

where $L^{-1} x_i$ is the probability of i at γ_i, and $r = \gamma + k - \gamma$.

For our binary mixture we define four f_{ij}'s

$$f_{11}(\gamma_1, \gamma_1') = f_{11}(-\gamma_1', -\gamma_1) \quad , \tag{1.19}$$

$$f_{22}(\gamma_2, \gamma_2') = f_{22}(-\gamma_2', -\gamma_2) \quad , \tag{1.20}$$

and

$$f_{12}(\gamma_1, \gamma_2') = f_{21}(-\gamma_2', -\gamma_1) \quad . \tag{1.21}$$

We also define one-point probability density functions $f_i(\gamma_i)$ such that

$$f_i(\gamma_i) = \int_{-k+\gamma_i}^{L-k+\gamma_i} d\gamma_i' f_{ii}(\gamma_i, \gamma_i') + \int_{-k+\gamma_i}^{L-k+\gamma_i} d\gamma_j' f_{ij}(\gamma_i, \gamma_j') \quad , \tag{1.22}$$

subject to the normalization

$$x_i = \int_{-L/2}^{L/2} d\gamma_i f_i(\gamma_i) \quad , \tag{1.23}$$

and symmetry

$$f_i(\gamma_i) = f_i(-\gamma_i) \quad . \tag{1.24}$$

In equation (1.22) $j \neq 1$, and $k = L/M = 1/\rho$.

The configurational entropy and internal energy are then given by[8]

$$S/k_B M = \sum_{i=1}^{2} \left[\int_{-L/2}^{L/2} d\gamma_i f_i (\gamma_i) \ln f_i (\gamma_i) \right.$$

$$\left. - \int_{-L/2}^{L/2} d\gamma_i \int_{-k+\gamma_i}^{L-k+\gamma_i} d\gamma_i f_{ii}(\gamma_i, \gamma_i') \ln f_{ii}(\gamma_i, \gamma_i') \right]$$

$$-2 \int_{-L/2}^{L/2} d\gamma_1 \int_{-k+\gamma_1}^{L-k+\gamma_1} d\gamma_i \, f_{12}(\gamma_1, \gamma_2') \ln f_{12} (\gamma_1, \gamma_2') \quad ,$$

and

$$E/M = \sum_{i=1}^{2} \left[\int_{-L/2}^{L/2} d\gamma_i \int_{-k+\gamma_i}^{L-k+\gamma_i} d\gamma_i' \, \phi_{ii}(\gamma_i, \gamma_i') \, f_{ii}(\gamma_i, \gamma_i') \right]$$

$$+ 2 \int_{-L/2}^{L/2} d\gamma_1 \int_{-k+\gamma_1}^{L-k+\gamma_1} d\gamma_2' \quad \phi_{12} (\gamma_1, \gamma_2') \, f_{12}(\gamma_1, \gamma_2') \quad . \tag{1.26}$$

We can now construct the free energy F = E-TS and minimize F with respect to $f_i(\gamma_i)$ and $f_{ij}(\gamma_i, \gamma_j')$ under the restrictions of equations (1.19-1.24). Using the method of Lagrange undetermined multipliers (see Appendix A for the details of the calculation) we arrive at Kikuchi's result[8]

$$\frac{L}{x_1} f_{11}(r) = \frac{\Gamma - 1 + 2x1}{\Gamma + 1} \exp \left[\beta\mu_{11} - \beta pr - \beta\Phi_{11}(r) \right] \quad , \tag{1.27}$$

$$\frac{L}{x_2} f_{22}(r) = \frac{\Gamma + 1 - 2x_1}{\Gamma + 1} \exp \left[\beta\mu_{22} - \beta pr - \beta\Phi_{22}(r) \right] \quad , \tag{1.28}$$

$$\frac{L}{x_1} f_{12}(r) = \frac{2(1-x_1)}{\Gamma + 1} \exp \left[\beta\mu_{12} - \beta pr - \beta\Phi_{12}(r) \right] \quad , \tag{1.29}$$

and

$$\frac{L}{x_2} f_{21}(r) = \frac{2 x_1}{\Gamma + 1} \exp \left[\beta\mu_{21} - \beta pr - \beta\Phi_{21}(r) \right] \quad , \qquad (1.30$$

where

$$x_2 = 1 - x_1 \quad , \tag{1.31}$$

$$\Gamma^2 = 1 + 4x_1x_2(e^{\beta\omega(\xi)}-1) \quad ,$$

$$\omega(\xi) = 2\mu_{12}(\xi) - \mu_{11}(\xi) - \mu_{22}(\xi),$$

$$\xi = \beta p = p/kT \quad , \tag{1.32}$$

and $\Phi_{ij}(r) = \emptyset_{ij}(\gamma, \gamma')$.

Now define $e^{-\beta\mu_{ij}} \equiv \int_0^\infty e^{-\xi r} e^{-\beta\emptyset_{ij}(r)} dr.$ (1.33)

Taking Laplace transforms and using eqs. (1.18) and (1.33) we have

$$P_{11}(\sigma) = \frac{\Gamma - 1 + 2x_1}{\Gamma + 1} \frac{J_{11}(\xi+\sigma)}{J_{11}(\xi)} \quad , \tag{1.34}$$

$$P_{12}(\sigma) = \frac{2x_2}{\Gamma + 1} \frac{J_{12}(\xi+\sigma)}{J_{12}(\xi)} \quad , \tag{1.35}$$

$$P_{21}(\sigma) = \frac{2x_1}{\Gamma + 1} \frac{J_{21}(\xi+\sigma)}{J_{21}(\xi)} \quad , \tag{1.36}$$

and

$$P_{22}(\sigma) = \frac{\Gamma + 1 - 2x_1}{\Gamma + 1} \frac{J_{22}(\xi+\sigma)}{J_{22}(\xi)} \quad , \tag{1.37}$$

where now J(x) is the Laplace transform of the Boltzmann factor given by

$$J_{ij}(x) = \int_0^\infty e^{-xt} e^{-\beta\emptyset_{ij}(t)} dt \quad . \tag{1.38}$$

Substituting (1.34-1.37) into equation (1.15) gives

$$1 - C_{11}J_{11}(\xi+\sigma)/J_{11}(\xi) - C_{22}J_{22}(\xi+\sigma)/J_{22}(\xi)$$
$$+ C_{11}C_{22}J_{11}(\xi+\sigma)J_{22}(\xi+\sigma)/J_{11}(\xi)J_{22}(\xi)$$
$$- C_{21}C_{12}J_{21}(\xi+\sigma)J_{12}(\xi+\sigma)/J_{21}(\xi)J_{12}(\xi) = 0, \quad (1.39$$

with

$$C_{11} = (\Gamma-1+2x_1)/(\Gamma+1) \quad , \quad (1.40)$$

$$C_{22} = (\Gamma+1-2x_1)/(\Gamma+1) \quad , \quad (1.41)$$

$$C_{21} = 2x_1/(\Gamma+1) \quad , \quad (1.42)$$

and $$C_{12} = 2x_2/(\Gamma+1) \quad . \quad (1.43)$$

We shall now proceed to solve equation (1.39) for various types of intermolecular pair potentials.

EQUATION OF STATE

Before proceeding further to solve equation (1.39) we first derive the equation of state for our model mixtures.[8]

From appendix A equation (1.σ9) we have

$$-F/Mk_BT = \xi k + \ln(\Gamma+1) - x_1(\beta\mu_{11} + \ln(\Gamma-1+2x_1)$$
$$-x_2(\beta\mu_{22} + \ln(\Gamma+1-2x_1)) \quad .$$

ξ is determined from the condition that F of equation (1.29) is made a minimum with respect to ξ, keeping k and T constant. Then one obtains the equation of state:

$$\rho^{-1} = \frac{\partial}{\partial\xi}\ (\ln(\Gamma+1) - x_1(\beta\mu_{11} + \ln)(\Gamma-1+2x_1)$$
$$-x_2(\beta\mu_{22} + \ln(\Gamma+1-2x_1))). \tag{2.1}$$

Or, using equation (1.33) we have

$$-\rho^{-1} = x_1 J_{11}'(\xi)/J_{11}(\xi) + x_2 J_{22}'(\xi)/J_{22}(\xi) + \frac{\partial}{\partial\xi}\ C \quad , \tag{2.2}$$

where $\qquad C = -\ln(\Gamma+1) + x_1\ln(\Gamma-1+2x_1) + x_2\ln(\Gamma+1-2x_1)$, (2.3)

and where the prime denotes differentiation of the function with respect to its argument.

Equation (2.2) is in agreement with the work of Lebowitz and Zomick[6] and C.C. Carter[9] for the case of an hard-sphere interaction. In the simple fluid limit equation (2.2) agrees with the work of Katsura and

Tage[10] for a system with a square-well interaction. (see appendix C for details of the comparison.)

HARD-SPHERE CALCULATIONS

Let $\phi_{ij}(r)$ be a hard-sphere potential given by

$$\phi_{ij}(r) = \infty \quad r < b_{ij} \tag{3.1}$$
$$= 0 \quad r \geq b_{ij} \quad ,$$

where

$$b_{11} = b \quad ,$$

$$b_{22} = Nb \quad ,$$

and
$$b_{12} = b_{21} = (N+1)b/2 \quad .$$

First we need the value of Γ given by

$$\Gamma^2 = 1 + 4x_1 x_2 (e^{\beta\omega(\xi)} - 1) \quad ,$$

where
$$\omega(\xi) = 2\mu_{12}(\xi) - \mu_{11}(\xi) - \mu_{22}(\xi),$$

and
$$e^{-\beta\mu_{ij}(\xi)} = \int_0^{\infty} e^{-\xi r - \beta\phi_{ij}(r)} \, dr \quad .$$

Thus
$$e^{\beta\omega(\xi)} = J_{11}(\xi) J_{22}(\xi) / (J_{12}(\xi))^2 \quad . \tag{3.2}$$

The Boltzmann factors are given by

$$J_{11}(\xi) = \int_0^{\infty} e^{-\xi r - \beta\phi_{11}(r)} dr = \int_0^{b} e^{-\xi r} e^{-\infty} dr + \int_b^{\infty} e^{-\xi r} e^{-0} dr$$
$$= -\frac{1}{\xi} e^{-\xi r} \Big|_b^{\infty}$$
$$= \frac{e^{-\xi b}}{\xi} \quad , \tag{3.3}$$

$$J_{22}(\xi) = \int_0^\infty e^{-\xi r}\, e^{-\beta\phi_{22}(r)} dr = \int_0^{Nb} e^{-\xi r} e^{-\infty} dr \int_{Nb}^\infty e^{-\xi r} e^{-0}\, dr$$

$$= \frac{e^{-Nb\xi}}{\xi} \quad , \tag{3.4}$$

and $$J_{12}(\xi) = \int_0^{\frac{N+1}{2}b} e^{-\xi}\, e^{-\infty} dr + \int_{\frac{N+1}{2}b}^\infty e^{-\xi r}\, e^{-0}\, dr$$

$$= \frac{e^{-\frac{N+1}{2}b\xi}}{\xi} \quad . \tag{3.5}$$

Thus $$e^{\beta\omega(\xi)} = \frac{\frac{1}{\xi} e^{-\xi b}\ \frac{1}{\xi} e^{-N\xi b}}{\left[\frac{1}{\xi}\ e^{-\frac{N+1}{2}b\xi}\right]^2} \quad .$$

Therefore $\Gamma^2 = 1$ and $\Gamma = 1$. (Γ is defined as $+\ (\Gamma^2)^{1/2}$)

We then have,

$$P_{11}(\sigma) = x_1 \xi e^{-\sigma b}/(\xi + \sigma) \quad , \tag{3.6}$$

$$P_{12}(\sigma) = x_2 \xi e^{-\frac{\sigma b}{2}(N+1)}/(\xi + \sigma) \quad , \tag{3.7}$$

$$P_{21}(\sigma) = x_1 \xi e^{-\frac{\sigma b}{2}(N+1)}/(\xi + \sigma) \quad , \tag{3.8}$$

and $$P_{22}(\sigma) = x_2 \xi e^{-\sigma N b}/(\xi + \sigma) \quad , \tag{3.9}$$

Thus $P_{11}P_{22}$ cancel and equation (1.39) reduces to

$$u(x_1 e^{-\lambda} + (1-x_1)e^{-N\lambda}) = u + \lambda \quad , \tag{3.10}$$

where $\lambda = b\sigma$ and $u = b\xi$.

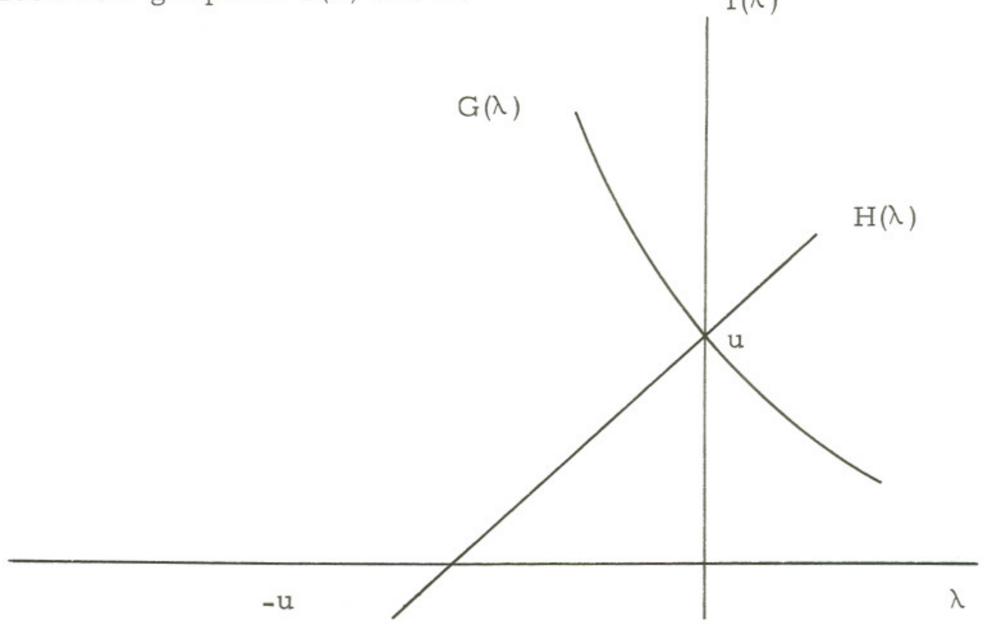
Equation (3.10) is in exact agreement with the work of C.C. Carter[9] on the hard-sphere limit of a van der Waal's mixture.

Now let

$$G(\lambda) = u(x_1 e^{-\lambda} + (1-x_1)e^{-N\lambda}) = f(\lambda)$$

and $$H(\lambda) = u + \lambda = f(\lambda)$$

and look at a graph of $f(\lambda)$ vs. λ.



Since the only crossing is at $\lambda = 0$, there are no non-zero real roots of equation (3.10). The decay of G(r) will then be determined by the complex root of least negative real part. The pair correlation function will decay as a damped sinusoid with the real part of the root determining the damping and the imaginary part determining the frequency of the spatial oscillation.

We shall now proceed to solve equation (3.10) both analytically, using a technique developed by Fisher and Widom[1], and numerically using the Muller's method[11] technique. First the analytical solution. Let N = 1 in equation (3.10) and we generate the equation for a simple fluid

$$ue^{-\lambda} = \lambda + u \quad . \tag{3.11}$$

Now rewrite equation (3.11) as

$$e^{-u}e^{-\lambda} = (e^{-u}/u)(\lambda + u)$$

and define $\zeta = \lambda + u$ and $\lambda_o = e^{-u}/u$. This gives

$$e^{-\zeta} = \lambda_o\zeta \quad . \tag{3.12}$$

Now let $\zeta = x + iy$ with x and y real. Then

$$e^{-x}(\cos y - i\sin y) = \lambda_o(x \quad iy)$$

$$e^{-x}\cos y = \lambda_o x \tag{3.13}$$

$$e^{-x}\sin y = -\lambda_o y \tag{3.14}$$

Now multiply equation (3.14) by coty. This gives

$$e^{-x}\cos y = \lambda_o x = \lambda_o \cot y \quad . \tag{3.15}$$

We now note that equation (3.15) has extraneous roots when x = 0 while cosy = ycoty = 0. Also, the second of equations (3.15) is spurious when y = 0. We also note the special case x = 0, cosy = 0, while

$\lambda_o = ((2n + 3/2\,\pi)^{-1}$. From the second and third members of (3.15) we have

$$x = -y\cot y, \tag{3.16}$$

while the first and third parts give

$$e^{-x}\cos y = \lambda_o y\cot y \quad ,$$
$$\cos y = \lambda_o y\cot y e^{x} \quad . \tag{3.17}$$

Or, using equation (3.16) in equation (3.17), then gives

$$\cos y = -\lambda_o y\cot y e^{-y\cot y} \quad . \tag{3.18}$$

We shall call equation (3.18) the indicial. The indicial is shown if Figure (1) for the case $\lambda_o = .368$. (This value corresponds to u = 1.) Independently of (3.18) cosy is a certain many valued function of ycoty. Each branch of this function may be labeled by an index ν such that $\pi\nu < y < (\nu+1)\pi$ on the branch. The first several branches of this function are also shown in Figure (1). The roots of equation (3.18) are then given by the intersections of the indicial with one of the infinitely many branches of cosy = f(ycoty). From (3.16) one can see that the smaller ycoty will correspond to the larger x. The intersections at the origin are the extraneous roots mentioned earlier. The branches of cosy = f(ycoty) pass through the origin with slope $m = (-1)^{\nu}/(\nu + \frac{1}{2})\pi$ on the branch of index ν, while the indicial passes through the origin with slope $m = -\lambda_o$. Thus the intersection occurring at the smallest value of ycoty will always be the

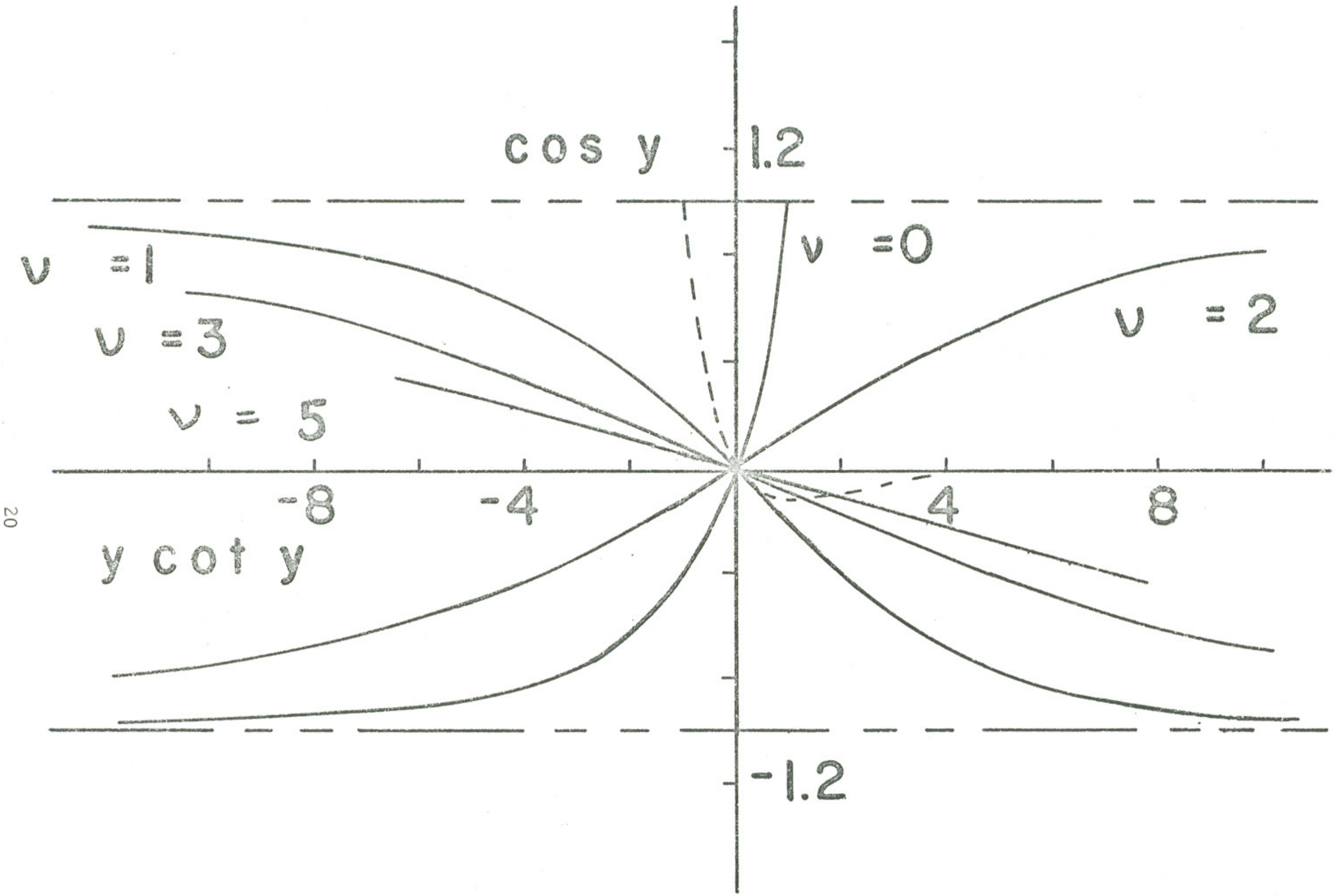


Figure 1

intersection of the indicial with the ν = 1 branch of cosy = f(ycoty). Thus equation (3.11) has a unique complex root of least negative real part. From Figure (1) we can read the values of λ_1, λ_2, and λ_3 and we have

$$\lambda_1 = -1.50 + i\ 4.65$$

$$\lambda_2 = -2.35 + i\ 10.85$$

and

$$\lambda_3 = -2.87 + i\ 17.15 \quad .$$

Numerical solution of equation (3.11) gives

$$\lambda_1 = -1.53 + i\ 4.60 \quad ,$$

$$\lambda_2 = -2.40 + i\ 10.80$$

and

$$\lambda_3 = -2.85 + i\ 17.17 \quad .$$

Now let N = 2 in equation (3.10)

$$(u(x_1 e^{-\lambda} + (1-x_1)\, e^{-2\lambda}) = u + \lambda \tag{3.19}$$

$$e^{-\lambda}\ ((1-x_1)e^{-\lambda} + x_1) = (u + \lambda)/u$$

$$e^{-\tau} e^{-\lambda}\ ((1-x_1)e^{-\lambda}/x_1 + 1) = (1/x_1 u)e^{-\tau}\ (u + \lambda).$$

Now define

$$e^{-\tau} = (1-x_1)/x_1 \tag{3.20}$$

$$\lambda_o = (1/x_1 u)e^{-\tau} \tag{3.21}$$

$$a = u - \tau \tag{3.22}$$

and

$$\zeta = \lambda + \tau \quad . \tag{3.23}$$

Substituting equations (3.20-3.23) into equation (3.19) we have

$$e^{-\zeta}\ (e^{-\zeta} + 1) = \lambda_o\ (\zeta + a) \quad . \tag{3.24}$$

Now let $\zeta = x + iy$, x and y real and equation (3.24) becomes the pair

$$e^{-2x}\cos 2y + e^{-x}\cos y = \lambda_o(x+\alpha) \quad ,$$
$$e^{-2x}\sin 2y + e^{-x}\sin y = -\lambda_o y \quad ,$$

or, after some trigonometry, we have

$$e^{-2x}(2\cos^2 y - 1) + e^{-x}\cos y = \lambda_o(x+\alpha) \quad , \tag{3.25}$$

and
$$e^{-2x}(2\sin y\cos y) + e^{-x}\sin y = -\lambda_o y. \tag{3.26}$$

Multiply equation (3.26) by coty giving

$$2e^{-2x}\cos^2 y + e^{-x}\cos y = e^{-2x} + \lambda_o(x+\alpha) = -\lambda_o y\cot y \quad . \tag{3.27}$$

Again we have introduced extraneous roots. This time when x satisfies $e^{-2x} + \lambda_o(x+\alpha) = 0$, while $\cos y = y\cot y = 0$. Also the last equality in equation (3.27) is spurious when $y = 0$. From the second and third members of equation (3.27) we have

$$e^{-2x} + \lambda_o x = -\lambda_o y\cot y - \lambda_o \alpha \quad ,$$

or
$$\lambda_o^{-1}e^{-2x} + x = -y\cot y - \alpha \quad ,$$

or
$$(\lambda_o^{1/2}e^x)^{-2} + \ln \lambda_o^{1/2}e^x = -y\cot y - \alpha + \ln \lambda_o^{1/2} \quad . \tag{3.28}$$

Equation (3.28) can be written as

$$\lambda_o^{1/2}e^x = h(-y\cot y - \alpha + \ln\lambda_o^{1/2}) \quad , \tag{3.28}$$

where h is defined to be the smallest real solution of

$$(h(t))^{-2} + \ln(h(t)) = t \quad . \tag{3.29}$$

Now let $q = h^{-1}$

$$q^2 - \ln q = -s - \alpha + \ln \lambda_o^{1/2}$$

$$\ln q = q^2 + s + \alpha - \ln \lambda_o^{1/2}$$

$$q = e^{q^2 + s + \alpha - \ln \lambda_o^{1/2}}$$

$$q = e^{q^2 + A} \tag{3.30}$$

where $A = s + \alpha - \ln \lambda_o^{1/2}$. Equation (3.30) is plotted in Figure (2) as $q = f(q) = e^{q^2 + A}$. For a real solution to equation (3.30) to exist $f(q) = q$ and $f(q) = e^{q^2 + A}$ must cross. To find the value of A which makes the curves just tangent we differentiate and set the slopes equal to each other. Thus we have

$$\frac{df}{dq}(q) = \frac{d}{dq}(q) = 1$$

$$\frac{d}{dq} f(q) = \frac{d}{dq}(e^{q^2 + A}) = 2qe^{q^2 + A} \quad ,$$

and thus

$$1 = sqe^{q^2 + A} \quad .$$

Now solving

$$1 = 2qe^{q^2 + A} \quad ,$$

and

$$q = e^{q^2 + A}$$

simultaneously, one obtains

$$q = \sqrt{2}/2$$

and

$$A = -0.855 \quad .$$

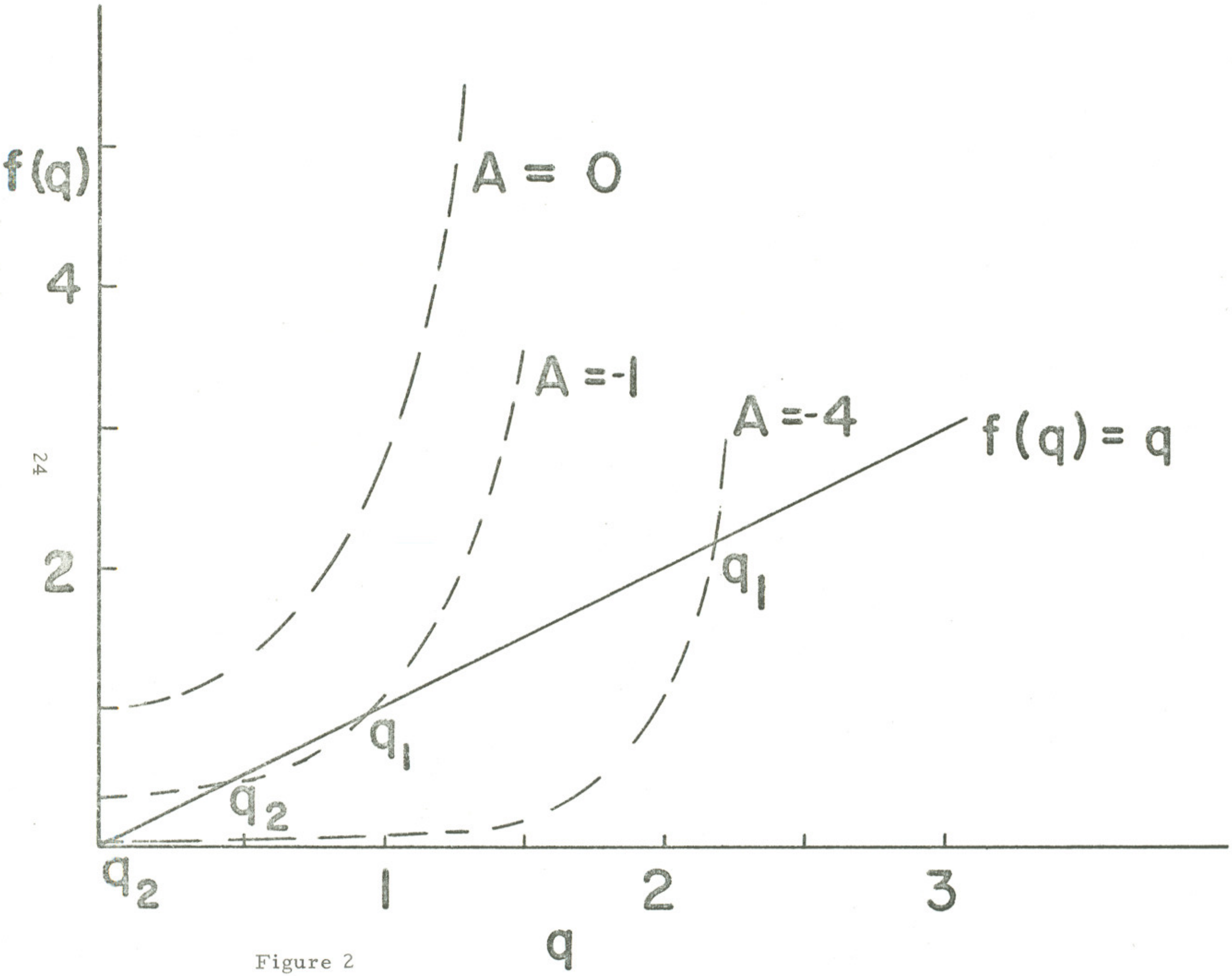


Figure 2

Thus for a real solution to equation (3.30) to exist A must be $< -.855$.

For all values of $A < -.855$

$$q_1 \to \infty \quad \text{as} \quad A \to -\infty \quad ,$$

and

$$q_2 \to 0 \quad \text{as} \quad A \to -\infty \quad ,$$

or

$$h_1 \to 0 \quad \text{as} \quad A \to -\infty \quad ,$$

and

$$h_2 \to \infty \quad \text{as} \quad A \to -\infty \quad .$$

h_1 is then the smallest real root. Also we have

$$A = s + \alpha - \ln \lambda_o^{1/2} < -.855 \quad ,$$

or

$$y \cot y < -(0.855 + \alpha - \ln \lambda_o^{1/2}) \quad . \tag{3.31}$$

From the first and third members of equation (3.27) we have

$$2e^{-2x} \cos^2 y + e^{-x} \cos y = -\lambda_o y \cot y ,$$

$$(4\cos y)^2 + 2e^x (4\cos y) + 8 \lambda_o s \, e^{2x} = 0 \quad ,$$

or

$$4\cos y = (-1 \pm (1 - 8 \lambda_o s)^{1/2}) e^x \quad ,$$

and using equation (3.28')

$$4\lambda_o^{1/2} \cos y = (-1 \pm (1 - 8\lambda_o y \cot y)^{1/2}) h(-y \cot y - \alpha + \ln \lambda_o^{1/2}) \quad . \tag{3.32}$$

Again we shall call equation (3.32) an indicial, and as before the intersections of the indicial with the various branches of $\cos y = f(y \cot y)$ will yield the solutions of equation (3.19). Figure (3) shows a plot of the indicial for the case $x_1 = 0.5$, $u = 1.0$. Also shown in the figure are the first few branches of $\cos y = f(y \cot y)$.

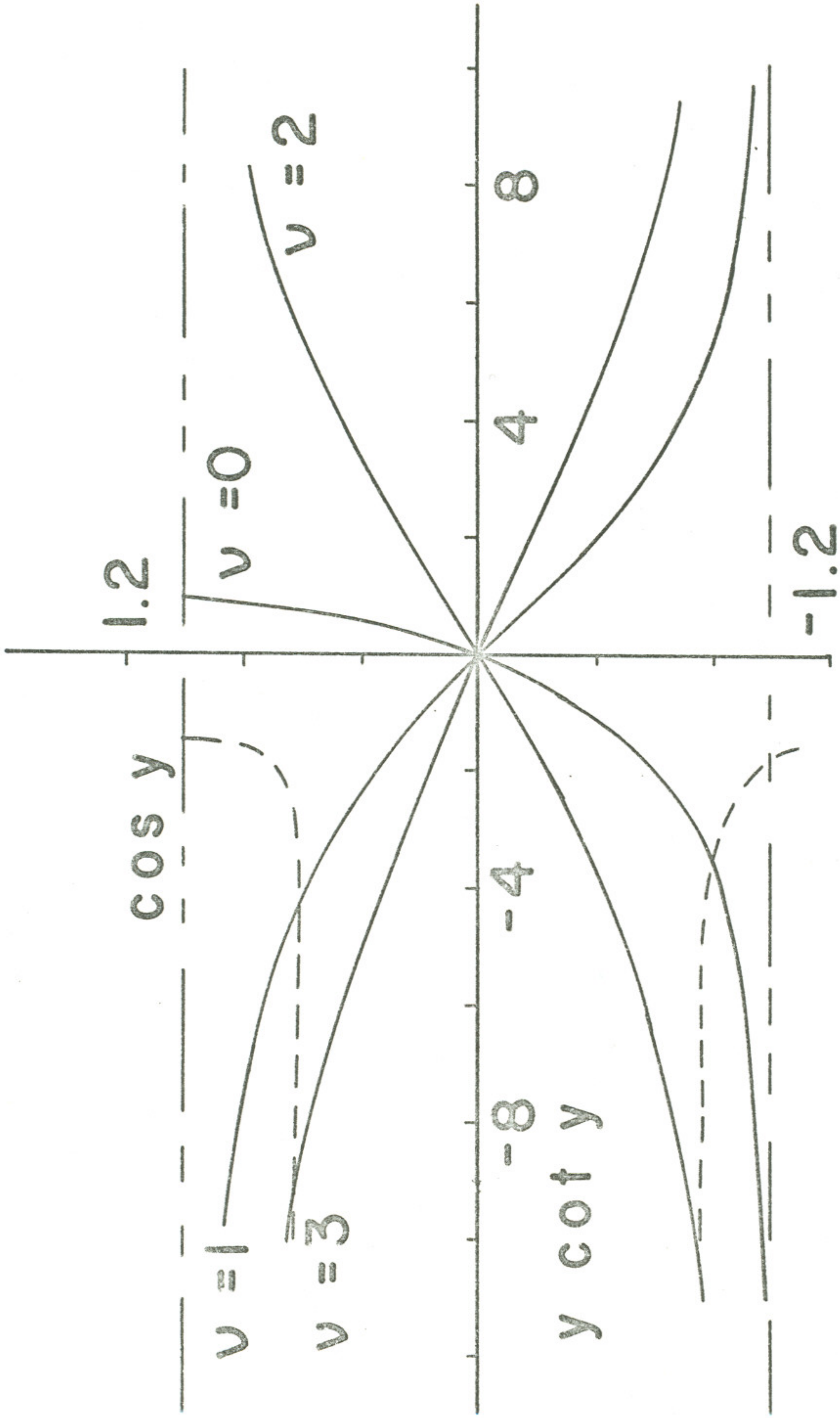


Figure 3

We now wish to see if equation (3.32) reduces properly in the simple fluid limit. Equation (3.32) came from solving the first and third members of equation (3.27) for 4cosy. If we use the definitions (3.21) and (3.23) and set $\lambda = \lambda_1 + i\lambda_2$; λ_1 and λ_2 real, we have, after multiplying through by $e^{-\tau}$ and setting $x_1 = 1$,

$$e^{-\lambda_1} \cos\lambda_2 = -\lambda_2 \cot\lambda_2/u \quad .$$

Setting $\lambda = \lambda_1 + i\lambda_2$; λ_1 and λ_2 real, in equation (3.12) and using equation (3.16), equation (3.18) gives

$$e^{-\lambda_1} \cos\lambda_2 = -\lambda_2 \cot\lambda_2/u \quad .$$

It must be noted that because equation (3.19) was multiplied through by $e^{-\tau}$, and this quantity goes to zero in the simple fluid limit, we must remove this factor before the limit can be taken. As we increase x_1, the mixture curves approach the simple fluid curve. However, since the mixture curves are dependent upon the logarithm of the concentration x_1 must be very near 1 before the curves will be similar. Figure (3-1) shows the curves for the simple fluid and for a mixture with x_1 equal to 0.5, 0.95, and 0.999. As x_1 increases the lower intersection (with $\nu = 0$ branch) moves out to -oo, and the upper intersection (with $\nu = 1$ branch) moves toward the simple fluid intersection.

From equation (3.28') and equation (3.29), it follows that the largest x will be associated with the largest ycoty.

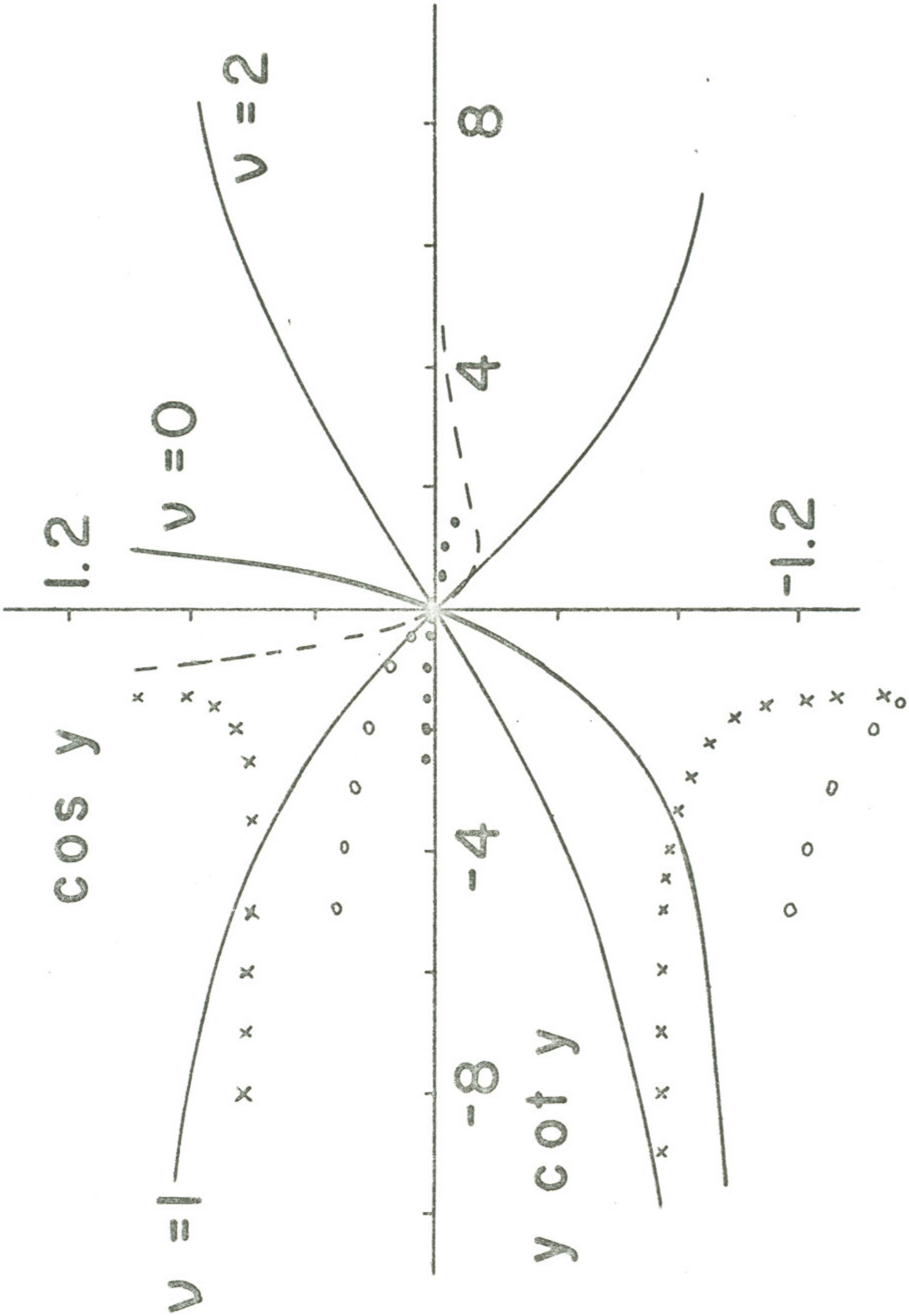


Figure 3-1

For the case shown in Figure (3) the two largest values of ycoty at an intersection are the ones associated with the $\nu = 0$ and $\nu = 1$ branches. This will always be the case since the branches of cosy = f(ycoty) pass through the origin with slope $m = (-1)^{\nu}/(\nu + \frac{1}{2})\pi$, and the slope of the indicials will always be greater than this, i.e. near the origin the indicials are more nearly vertical and above the cosy = f(ycoty) curves. (For values of ycoty near -0 the value of the indicial is always greater than the value of any of the cosy = f(ycoty) curves).

At the upper intersection

$$4\,\lambda_o^{1/2} K_1(\text{ycoty}) = (-1 + (1 - 8\,\lambda_o s)^{1/2})h, \tag{3.33}$$

where

$$\cos y = K_1(\text{ycoty})\ ; \quad \nu = 1 \text{ branch} \quad . \tag{3.34}$$

At the lower intersection

$$4\,\lambda_o^{1/2} K_2(\text{ycoty}) \quad (-1 - (1 - 8\,\lambda_o s)^{1/2})h \quad , \tag{3.35}$$

where

$$\cos y = K_2(\text{ycoty})\ ; \quad \nu = 0 \text{ branch} \quad . \tag{3.36}$$

Now let

$$K_1 = K_1\ (\text{ycoty}) \quad ,$$

and

$$K_2 = K_2\ (\text{ycoty}) \quad ,$$

then inverting equations (3.34) and (3.36) we have

$$K_2 \cos^{-1} K_2 / (1 - K_2^2)^{1/2} = -K_1 \cos^{-1} K_1 \,/(1 - K_1^2)^{1/2} \tag{3.37}$$

with

$$-1 < K_2 < 0 \quad \text{and} \quad 0 < K_1 < 1 \quad .$$

Now when the real parts of the two complex roots are equal we have, from equations (3.33) and (3.35),

$$K_1^{-1}(-1+(1-8\lambda_o s)^{1/2})h = K_2^{-1}(-1-(1-8\lambda_o s)^{1/2})h \quad ,$$

$$(1-8\lambda_o s)^{1/2} = (K_2-K_1)/(K_2+K_1) \quad ,$$

$$\lambda_o = K_1K_2/(2s(K_2+K_1)^2) \quad ,$$

but

$$s = K_2\cos^{-1}K_2/(1-K_2^2)^{1/2} \quad ,$$

so

$$\lambda_o = K_1(1-K_2^2)^{1/2}/2\cos^{-1}K_2(K_2+K_1)^2 \quad . \tag{3.38}$$

From equation (3.29) we have

$$h^{-2} + \ln h = -s - \alpha + \ln \lambda_o^{1/2} \quad ,$$

or

$$\alpha = -h^{-2} - \ln h - s + \ln \lambda_o^{1/2} \quad .$$

However,

$$h = 4\lambda_o^{1/2}K_1(-1+(1-8\lambda_o s)^{1/2})^{-1} \quad ,$$

$$= 4\lambda_o^{1/2}K_1(-1+(K_2-K_1)/(K_2+K_1))^{-1}$$

or

$$h = -2\lambda_o^{1/2}(K_2+K_1) \quad . \tag{3.39}$$

Then

$$\alpha = -(2\lambda_o^{1/2}(K_2+K_1))^{-2} - \ln(-2\lambda_o^{1/2}(K_2+K_1)) - K_2\cos^{-1}K2/(1-K_2^2)^{1/2} + \ln\lambda_o^{1/2},$$

or

$$\alpha = -\tfrac{1}{2}\cos^{-1}K_2(1+2K_1K_2)/K_1(1-K_2^2)^{1/2} - \ln(-2(K_1+K_2)) \quad . \tag{3.40}$$

Equations (3.38) and (3.40) together with equation (3.37) are parametric equations for the transition locus in the (λ_o, α) plane. This locus is shown in Figure (4). From Figure (3) we may read the values of λ_1 and λ_2 and we get

$$\lambda_1 = -1.04 + i\,2.45$$

$$\lambda_2 = -1.12 + i\,5.38 \quad .$$

Numerical solution of equation (3.19) gives

$$\lambda_1 = -0.97 + i\,2.52$$

$$\lambda_2 = -1.08 + i\,5.38 \quad .$$

Here λ_1 is the intersection with the $\nu = 0$ branch and λ_2 is the intersection with the $\nu = 1$ branch.

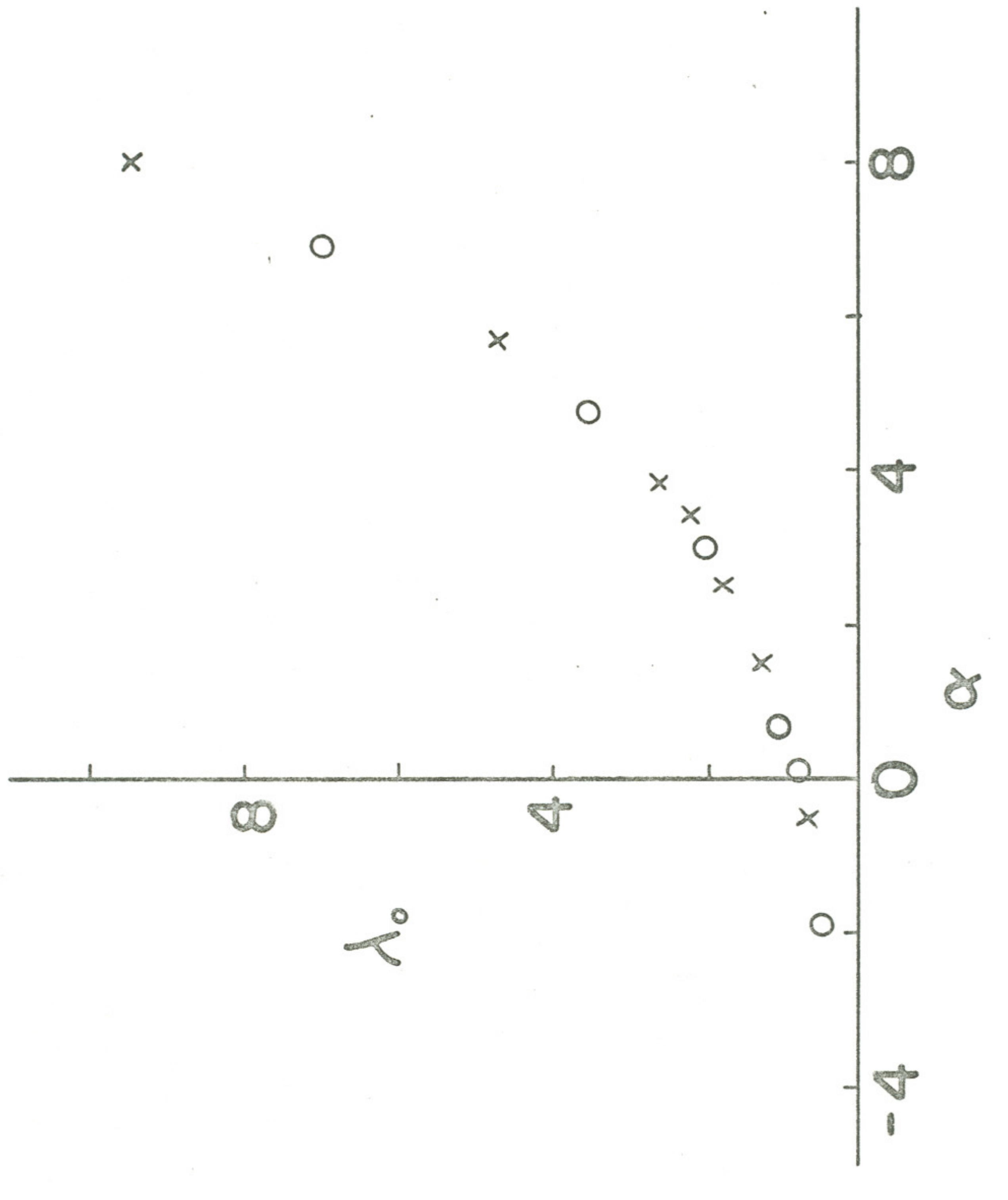


Figure 4

MULLER'S METHOD HARD SPHERES

Recall equation (3.10)

$$u(x_1e^{-\lambda} + (1-x_1)e^{-N\lambda}) = u + \lambda \quad .$$

This equation may be solved numerically using the Muller's method technique. Muller's method utilizes the following algorithm:

z_1, z_2, and z_3 are the initial guesses to the root. Now let

$$F1 = f(z_1) \quad ,$$

$$F2 = f(z_2) \quad ,$$

and

$$F3 = f(z_3) \quad ,$$

then the new guess is given by

$$z_{New} = z_3 + (z_3 - z_2)(-2F3\ )/(D \pm W) \quad ,$$

where

$$D = F1\,\lambda^2 - F2\,\delta^2 + F3\,(\lambda + \delta\,) \quad ,$$

$$W = (D^2 - 4F3\,\delta\,\lambda(F1\lambda - F2\delta + F3)) \quad ,$$

$$\delta = 1 + \lambda \quad ,$$

$$\lambda = (z_3 - z_2)/(z_2 - z_1) \quad ,$$

and the bottom sign is positive if $D + W > D - W$.

Convergence is then tested by

$$z_3 - z_{New} < C_1 \quad ,$$

where for our study $C_1 = 10^{-6}$. If the convergence criterion is not met let

$$z_1 = z_2$$

$$z_2 = z_3$$

$$z_3 = z_{New}$$

and try again.

When this method was applied to equation (3.10) using a UNIVAC 1108 computer the following results were obtained: Figure (5) shows a plot of the real parts of the two complex roots of largest real part. The dotted line is the locus of the complex root of least negative real part. Thus we see that the complex root of least negative real part changes abruptly as a function of u at constant x_1. Plots similar to Figure (5) can be made for various values of x_1 and we generate a locus in the (u, x_1) plane across which the asymptotic decay of the pair correlation function abruptly changes its spatial frequency. This locus is shown in Figure (6) for the case N = 2. The equation of state of our model mixture is given by equation (2.2)

$$-\rho^{-1} = x_1 J_{11}'(\xi)/J_{11}(\xi) + x_2 J_{22}'(\xi)/J_{22}(\xi) + \frac{\partial C}{\partial \xi} \quad .$$

For the hard sphere pair potential case we have for the Boltzmann factors

$$J_{11} = e^{-\xi b}/\xi \quad , \quad J_{11}' = (-e^{-\xi b}/\xi)(b + 1/\xi) \quad , \tag{4.1}$$

and
$$J_{22} = e^{-N\xi b}/\xi \quad , \quad J_{22}' = (-e^{-N\xi b}/\xi)(Nb + 1/\xi) \quad . \tag{4.2}$$

Since $\Gamma = 1$, C is a constant and $\frac{\partial C}{\partial \xi} = 0$.

Substituting these Boltzmann factors into equation (2.2) gives

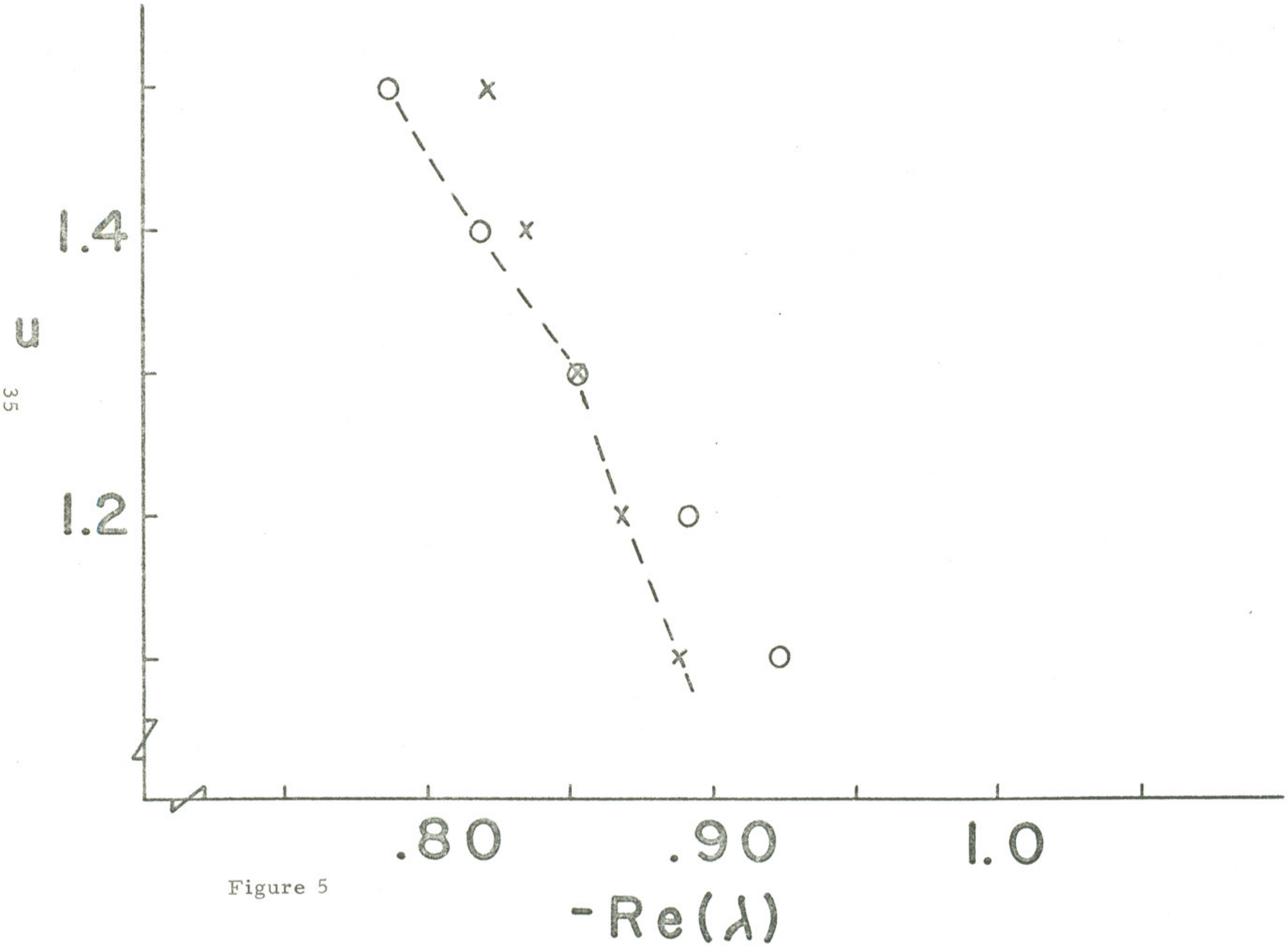


Figure 5

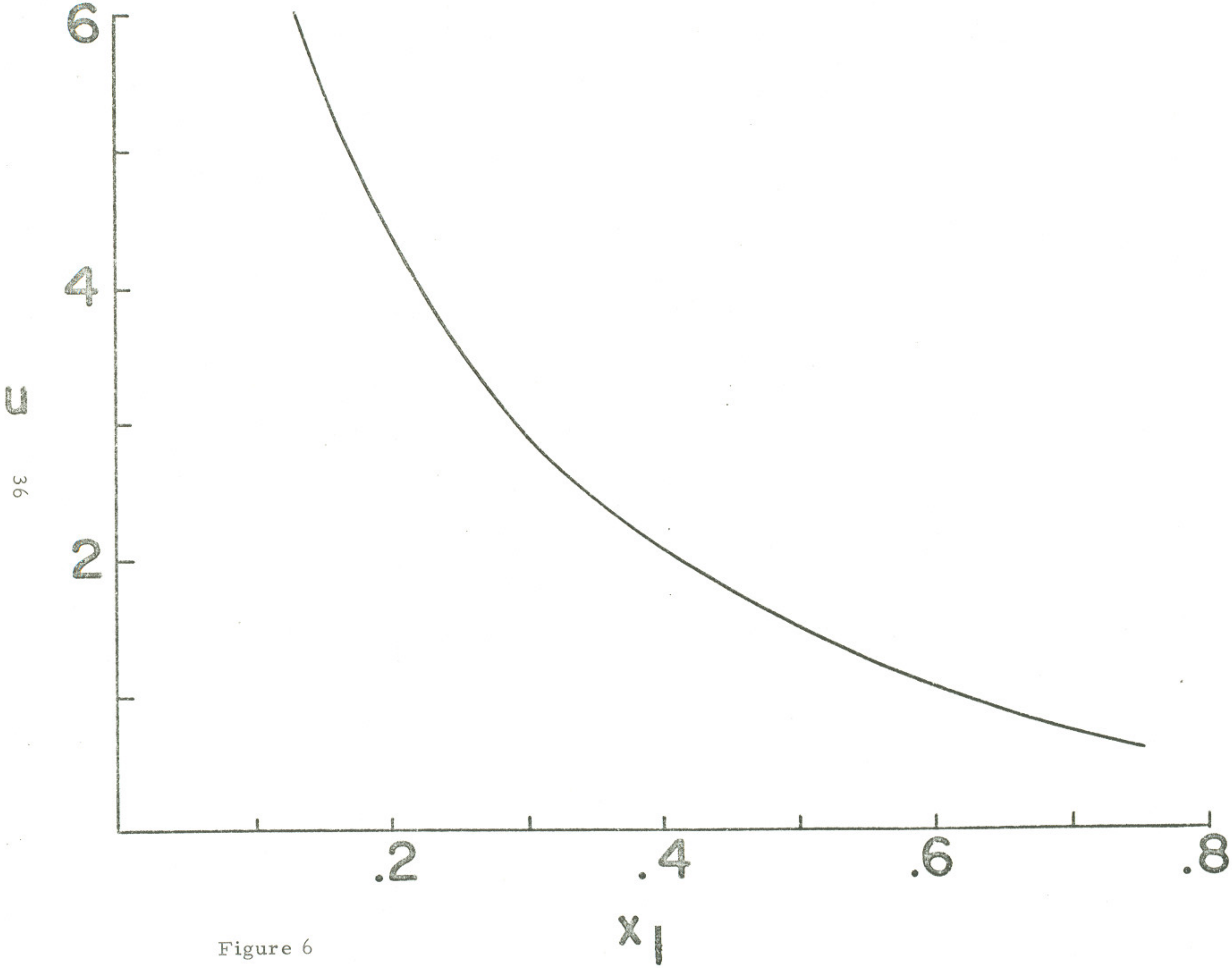


Figure 6

$$b\rho = u/u(1 + x_2(N-1)) + 1) \quad , \qquad (4.3)$$

where as usual $u = b\xi = pb/kT$.

Figure (7) shows the transition locus in the (ρ, x_1) plane for various values of the hard-core diameter ratio N.

Figure (8) shows the transition loci in the (ρ, N) plane for the cases $x_1 = .125$, .5, and .75. The dashed line is the limit of $b\rho$ as $x_1 \to 0$, $u \to \infty$.

$$\lim_{\substack{x_1 \to 0 \\ u \to \infty}} b\rho = \lim_{\substack{x_2 \to 1 \\ u \to \infty}} 1/(1+x_2(N-1)+1/u) \to 1/N \quad , \qquad (4.4)$$

which merely renormalizes the density, i.e. $\rho/\rho_{max.} = Nb\rho = 1$ when $pb/kT \to \infty$.

As x_1 approaches 1 the transition loci drop to zero because a simple fluid, i.e. $x_1 = 1$, has only one spatial frequency associated with the asymptotic decay of the pair correlation function.

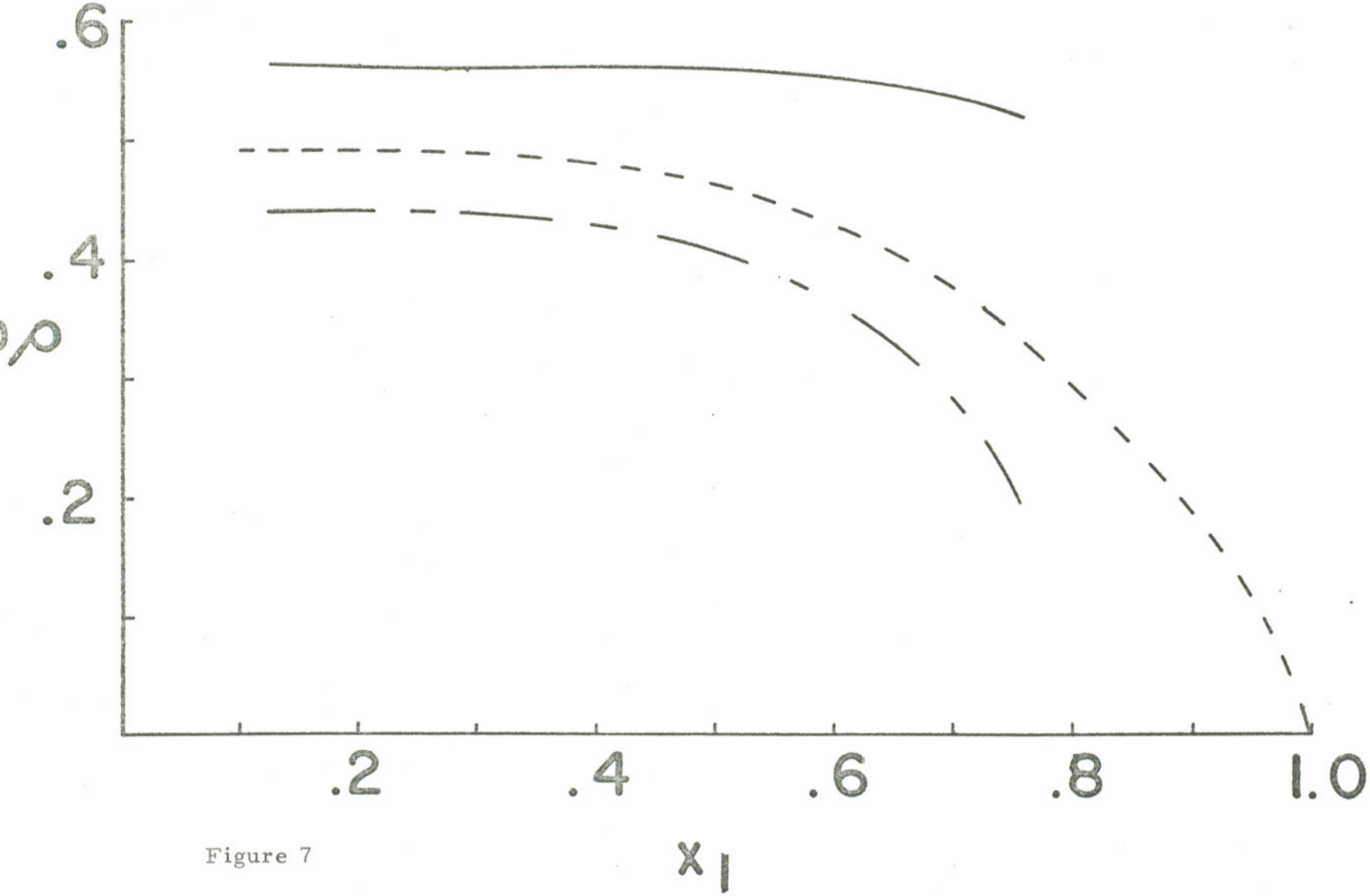


Figure 7

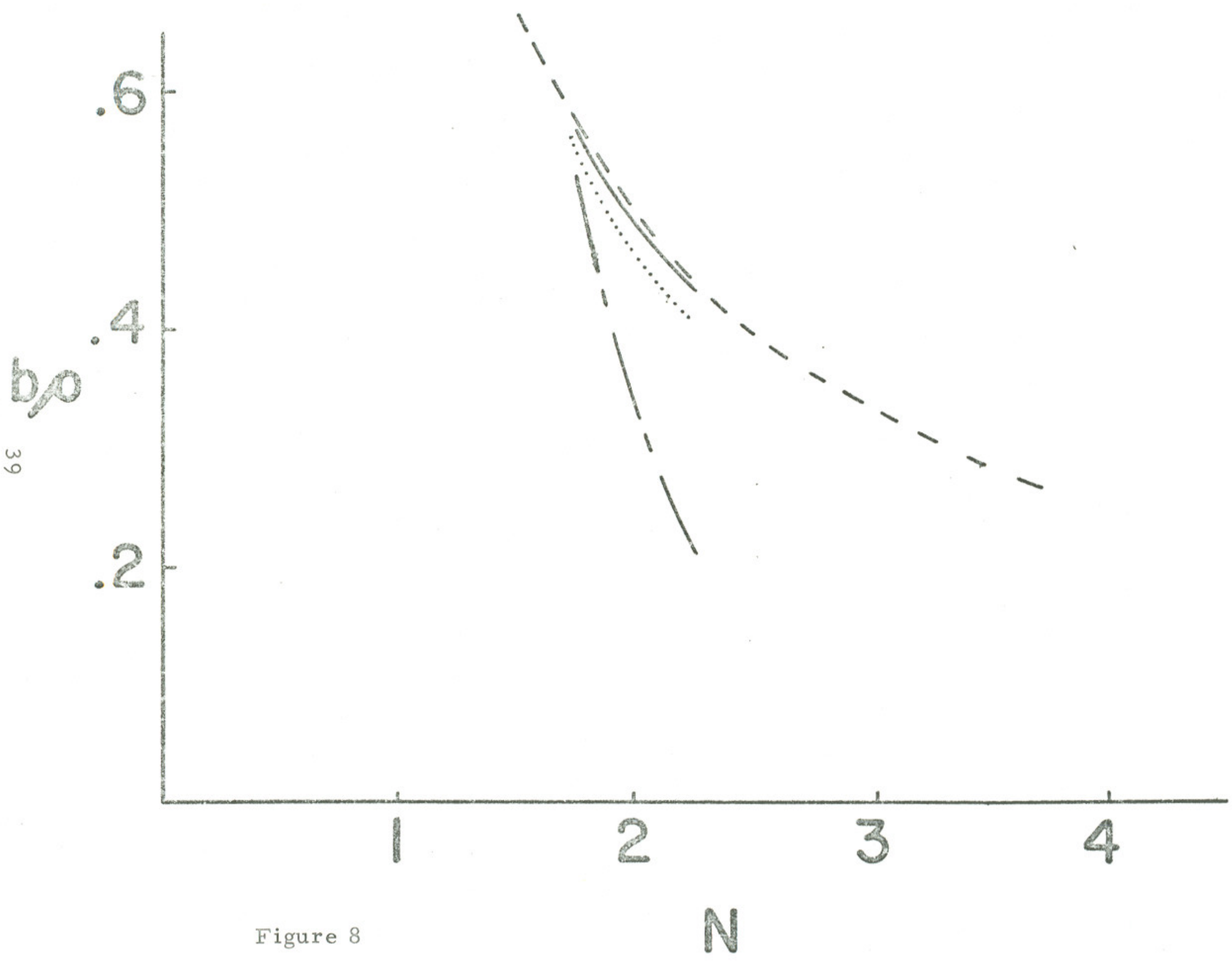
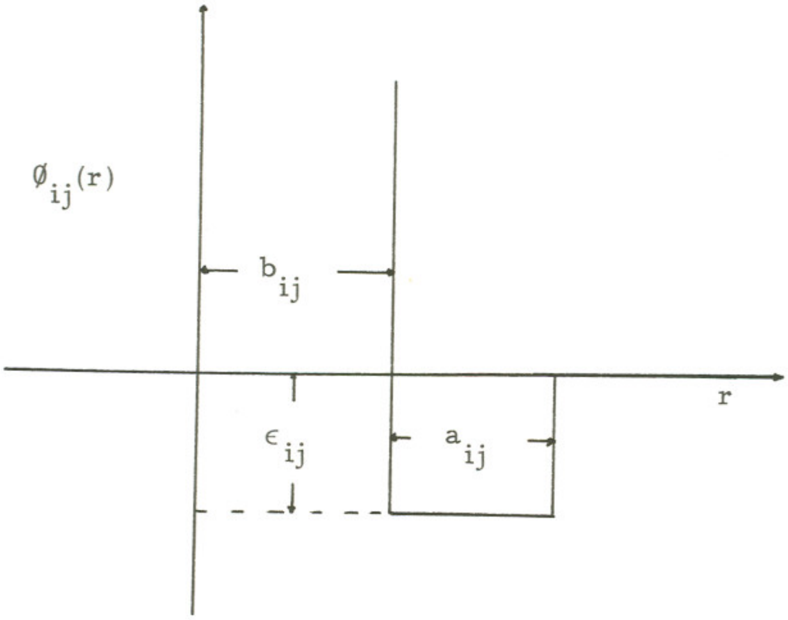


Figure 8

SQUARE-WELL POTENTIAL RESULTS

Let $\phi_{ij}(r)$ be a square-well potential given by



$$\begin{aligned} \phi_{ij}(r) &= \infty \quad r < b_{ij} \\ &= -\epsilon_{ij} \quad b_{ij} < r < a_{ij} + b_{ij} \\ &= 0 \quad r \geq b_{ij} + a_{ij} \end{aligned} \tag{6.0}$$

where b_{ij} = hard-core diameter, a_{ij} = well-width, and ϵ_{ij} = well-depth.
Furthermore let

$$\begin{aligned} a_{ij} &= Rb_{ij} \\ b_{BB} &= Nb_{AA} \\ b_{AB} &= \frac{(N+1)}{2}\, b_{AA} = Cb_{AA} \\ \epsilon_{BB} &= H\epsilon_{AA} \\ \epsilon_{AB} &= (H)^{1/2}\epsilon_{AA} \end{aligned}$$

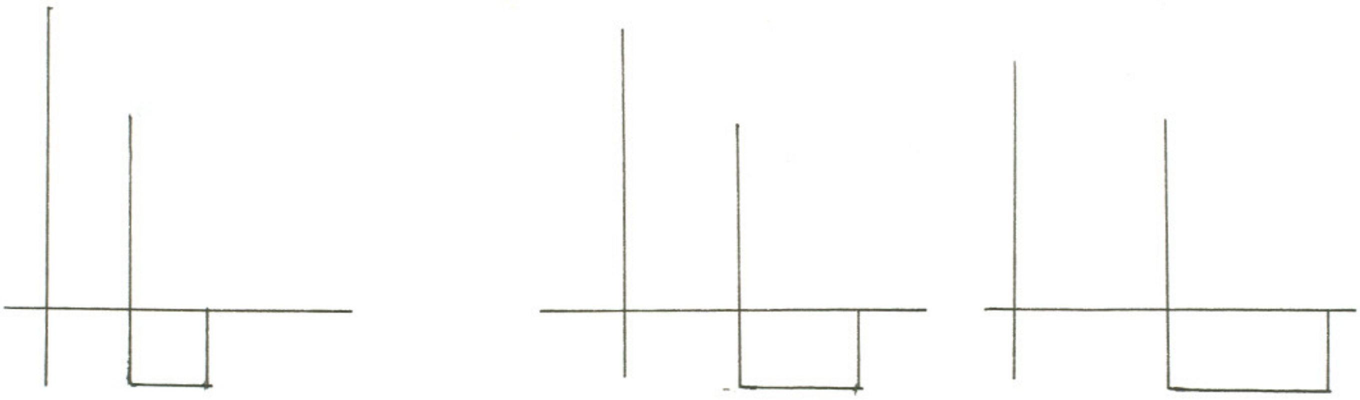
$$b_{AA} = b$$

$$\epsilon_{AA} = \epsilon \quad . \qquad (6.0')$$

SQUARE-WELL CASES

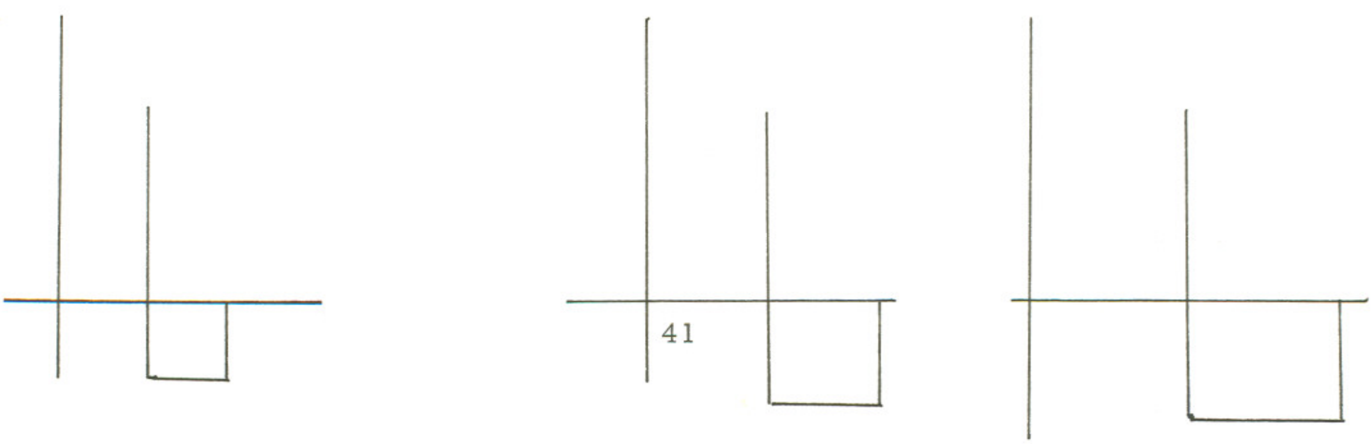
Case 1 N = 2 R = 1 H = 1

AA AB BB



Case 2 N = 2 R = 1 H = 1.5

AA AB BB



We now wish to derive an equation for the pole of least negative real part of the Laplace transform of the pair correlation function for a system interacting through a square-well intermolecular pair potential. First we need the value of Γ^2 given by

$$\Gamma^2 = 1 + 4x_1x_2(e^{\beta\omega(\xi)} - 1) \quad , \tag{6.1}$$

where

$$e^{\beta\omega(\xi)} = J_{11}(\xi)J_{22}(\xi)/(J_{12}(\xi))^2 \tag{6.2}$$

and the J_{ij}'s are the Laplace transforms of the Boltzmann factors. Now with $u = \xi b$, and $v = \beta\epsilon$, we have

$$J_{11} = (be^{v-u}/u)(1-e^{-Ru} + e^{-Ru-v}) \quad , \tag{6.3}$$

$$J_{22} = (be^{Hv-Nu}/u)(1-e^{-RNu} + e^{-RNu-Hv}) \, , \tag{6.4}$$

and

$$J_{12} = (be^{H^{1/2}v-Cu}/u)(1-e^{-CRu}+e^{-CRu-H^{1/2}v}) \quad . \tag{6.5}$$

Now let

$$J_{11} = (be^{v-u}/u)A_{11} \quad , \tag{6.6}$$

$$J_{22} = (be^{Hv-Nv}/u)A_{22} \quad , \tag{6.7}$$

and

$$J_{12} = (be^{H\ v-Cu}/u)A_{12} \quad , \tag{6.8}$$

where A_{11}, A_{22}, and A_{12} are defined from equations (6.3-6.5). Then

$$e^{\beta\omega} = \frac{((be^{v-u})/u)((be^{Hv-Nu})/u)A_{11}A_{22}}{(((be^{H^{1/2}v-Cu})/u)\ A_{12})^2}$$

$$= e^{V}A_{11}A_{22}/A_{12}^{\ 2} \quad , \tag{6.9}$$

with $$V = (H + 1 - 2H^{1/2})v \quad . \tag{6.10}$$

Now we must solve equation (1.15)

$$1 - P_{11} - P_{22} + P_{11}P_{22} - P_{21}P_{12} = 0 \quad . \tag{1.15}$$

The Boltzmann factors are given by

$$J_{11}(\xi + s) = \frac{be^{v-u}}{u + \lambda} \left(e^{-\lambda} - e^{-\lambda(R+1)-Ru} + e^{-\lambda(R+1)-Ru-v}\right) \quad , \tag{6.12}$$

$$J_{22}(\xi + s) = \frac{be^{Hv-Nu}}{u + \lambda} \left(e^{-N\lambda} - e^{-N(R+1)\lambda - RNu} + e^{-N(R+1)\lambda - RNu - Hv}\right) , \tag{6.13}$$

and

$$J_{12}(\xi + s) = \frac{be^{H\ v-Cu}}{u + \lambda} \left(e^{-C\lambda} - e^{-C(R+1)\lambda - RCu} + e^{-C(R+1)\lambda - RCu - H^{1/2}v}\right), \tag{6.14}$$

with $\lambda = bs$. Now define

$$C_{11} = (\Gamma - 1 + 2x_1)/(\Gamma + 1) \quad , \tag{6.15}$$

$$C_{22} = (\Gamma + 1 - 2x_1)/(\Gamma + 1) \quad , \tag{6.16}$$

$$C_{12} = 2x_2/(\Gamma + 1) \quad , \tag{6.17}$$

and

$$C_{21} = 2x_1/(\Gamma + 1) \quad . \tag{6.18}$$

Also let

$$J_{11}(\xi + s) = \frac{be^{v-u}}{u + \lambda} B_{11} \quad , \tag{6.19}$$

$$J_{22}(\xi + s) = \frac{be^{Hv-Nu}}{u + \lambda} B_{22} \quad , \tag{6.20}$$

and

$$J_{12}(\xi + s) = \frac{be^{H^{1/2}v-Cu}}{u + \lambda} B_{12} \tag{6.21}$$

Then substituting (6.15-6.20) into equation (1.15) and simplifying we have

$$u(C_{11}B_{11}/A_{11} + C_{22}B_{22}/A_{22} - (C_{11}C_{22}B_{11}B_{22}/A_{11}A_{22})(u/(u+\lambda))$$

$$+ (C_{21}C_{12}B_{12}^2/A_{12}^2)(u/(u+\lambda))) = u + \lambda \quad . \tag{6.21}$$

Further simplifying we have

$$u(T_{11} + T_{22} + T_3) = u + \lambda \quad , \tag{6.22}$$

where

$$T_3 = (u/u+\lambda)(4x_1x_2/(\Gamma+1)^2)\frac{(e^{-(N+1)\lambda})}{A_{12}^2}(D_{12}^2 - e^V D_{11}D_{22}) \quad , \tag{6.23}$$

$$T_{11} = C_{11}B_{11}/A_{11} \quad , \tag{6.24}$$

$$T_{22} = C_{22}B_{22}/A_{22} \quad , \tag{6.25}$$

$$D_{11} = e^{\lambda}B_{11} \quad , \tag{6.26}$$

$$D_{22} = e^{N\lambda}B_{22} \quad , \tag{6.27}$$

$$C \quad = (N+1)/2 \quad , \qquad (6.$$

and

$$D_{12} = e^{C\lambda}B_{12} \tag{6.28}$$

We shall now perform several checks on equation (6.22). First a check to see if it reduces to the correct simple fluid form. Let N = 1, R = 1, and H = 1, then

$A_{11} = A_{22} = A_{12}$, $B_{11} = B_{22} = B_{12}$ and

$V = 0$, $T_3 = 0$, $\Gamma = 1$.

Equation (6.22) then reduces to

$$u((B_{11}/A_{11})(C_{11} + C_{22})) = \lambda + u \quad ,$$

but

$$C_{11} + C_{22} = (\Gamma-1+2x_1 + \Gamma+1-2x_1)/(\Gamma+1) = 2\Gamma/(\Gamma+1) = 1 \quad ,$$

and thus our equation reduces to

$$uB_{11} = A_{11}\,(u+\lambda) \qquad (6.29)$$

Now let $x_1 = 1$. Then $\Gamma = 1$, $C_{11} = 1$, $C_{22} = 0$, $C_{12} = 0$, and $C_{21} = 1$. Thus equation (6.22) reduces to

$$uB_{11} = A_{11}\,(u+\lambda) \quad . \qquad (6.29)$$

Equation (6.29) is the correct simple fluid form.[1] Next we check the high temperature limit. Let $T \to oo$, then $v \to 0$ and $B_{11} \to e^{-\lambda}$, $B_{22} \to e^{-N\lambda}$, $B_{12} \to e^{-C\lambda}$, $B_{21} \to e^{-C\lambda}$, $A_{11} \to A_{22} \to A_{12} \to 1, \Gamma \to 1$, $C_{11} \to x_1$, $C_{22} \to x_2$, $C_{12} \to x_2$, and $C_{21} \to x_1$. Equation (6.22) then reduces to

$$u(x_1 e^{-\lambda} + (1-x_1)e^{-N\lambda}) = u + \lambda \quad . \qquad (6.29')$$

Equation (6.29') is the equation for a hard-sphere mixture. Next we check to make sure that the trivial root at $\lambda = 0$ is present. Setting $\lambda = 0$ we have

$$D_{ij} = A_{ij} = B_{ij}$$

Substituting these into equation (6.22) we have

$$u(2\Gamma/(\Gamma+1) \quad (1-\Gamma^2)/(1+\Gamma)^2\,) = u \quad ,$$

or

$$u(\Gamma+1)/(\Gamma+1) = u \; .$$

Thus the trivial root checks.

Let us now examine equation (6.22) to determine the nature of the non-trivial roots. First we rewrite the equation as

$$u(T_{11}(u+\lambda) + T_{22}(u+\lambda) + uT_3') = (u+\lambda)^2 \quad , \tag{6.30}$$

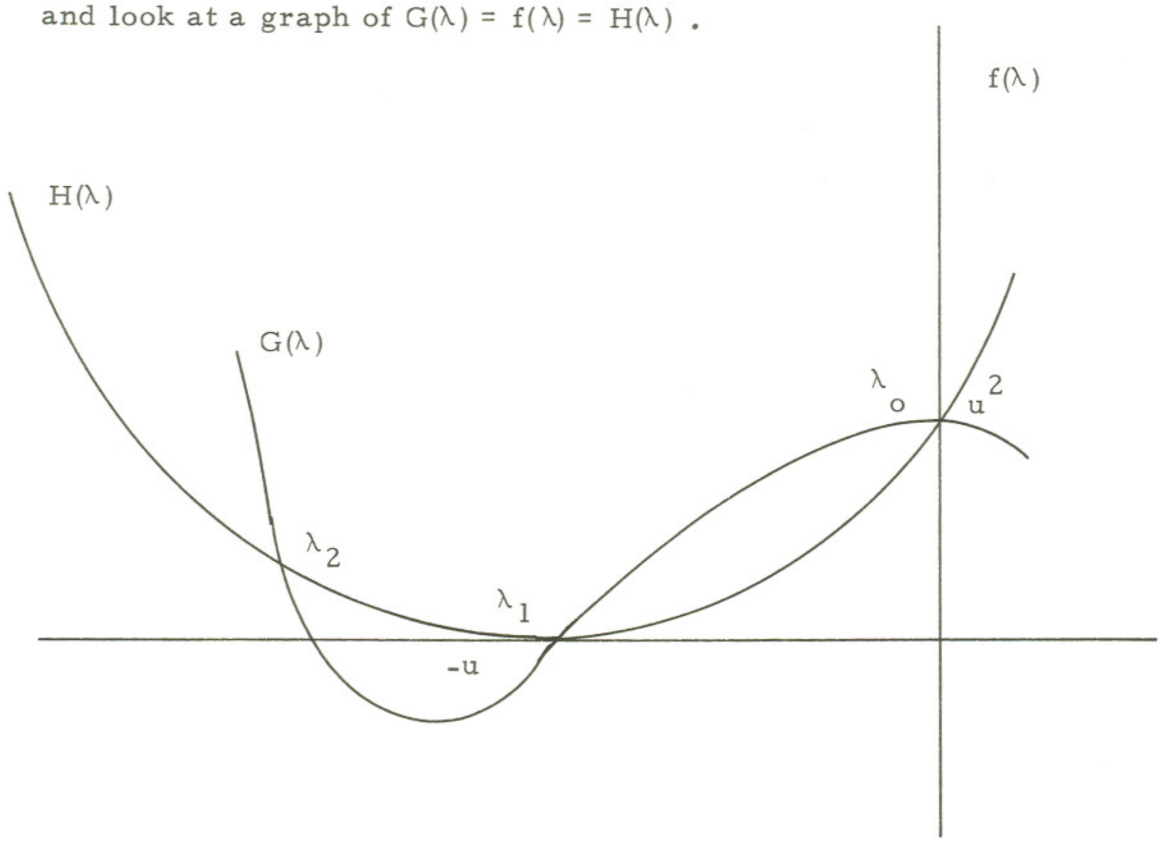
where $T_3' = ((u+\lambda)/u)\ T_3$.

Equation (6.30) will now have an extraneous root when $u + \lambda = 0$. Now set

$$G(\lambda) = u(T_{11}(u+\lambda) + T_{22}(u+\lambda) + uT_3')$$

and $$H(\lambda) = (u+\lambda)^2$$

and look at a graph of $G(\lambda) = f(\lambda) = H(\lambda)$.



Thus the roots of equation (6.22) are

$\lambda_o = 0$, the trivial root

$\lambda_1 = -u$, the extraneous root

$\lambda_2 = \lambda_R$, the relevant real root

and $\lambda_3 - \lambda_{oo} = \lambda_c$, the infinite set of complex roots.

Thus our square-well mixture will have one relevant real root and an infinite set of complex conjugate pairs of roots. Our task now is to determine which of the roots of equation (6.22) is the root of least negative real part.

MULLER'S METHOD SQUARE-WELL

Equation (6.22) was programmed in FORTRAN V for a UNIVAC 1108 computer using the Muller's method technique for extracting the roots. The program proceeds as follows: Appropriate values of the variables $u = bp/kT$ and $v = \epsilon/kT$ are read into arrays. The program then picks up the values of the parameters R, N, and H. Next the first Muller's method loop is executed with the restrictions that the extracted root is both real and negative. When found the root is set equal to Z1. The program then executes three more Muller's method loops with no restrictions on the roots. However, each time a root is found, both it and its complex conjugate are numerically divided out before the program proceeds to the extraction of the next root. The program begins searching for roots just off the x,y axis in the second quadrant of the complex plane, and each time a root is found the program attempts to find another root whose real part is greater, i.e. less negative.

Once four roots, one real and three complex (actually each complex root is a complex conjugate pair), have been extracted for a given set of u and v, the program picks the root of least negative real part and compares it with the root of least negative real part from the previous set of u and v. If the root is the same one, i.e. both real or both from the same complex branch, the program proceeds on to the next set of u and v. However, if the roots are different the program prints out both sets of roots along with the corresponding values of u and v. The entire program is then looped on various values of x_1.

Once the roots have been found they are put on paper tape and run into a BASIC program on a PDP-11 computer which does linear interpolation between the sets of u and v and then prints out the corresponding values of pressure, temperature, concentration, and density. Plots are then constructed in the (p, T) and (ρ, T) planes. From the (ρ, T) plots a cut at constant ρ is taken and a plot in the (T, x_1) plane is made. These plots are shown in Figures (9) through (14).

Figures (9.1) through (9.4) show the transition locus in the (p, T) plane for the cases $N = 2$, $R = 1$, $H = 1$, and $x_1 = .1, .4, .5,$ and $.8$. As the concentration of the smaller species increases the transition loci become more complex. At a concentration of 0.8 the plane is divided into four distinct regions. Each region is characterized by the spatial frequency of the oscillation of the damped sinusoid characterizing $G(r)$. The zero frequency region corresponds to monotonic exponential decay of the pair correlation function. We note that all all concentrations there exists a maximum pressure, above which, the decay is always oscillatory. This is in agreement with the results for a cimple fluid square-well.[1,3]

As the concentration of the smaller species increases the $\omega = 0$, $\omega \sim 3$, and $\omega \sim 4$ regions increase, while the $\omega \sim 2$ region decreases. Figures (10.1) through (10.4) show the transition loci in the (ρ, T) plane at constant x_1. Once again there is an enhancement of the $\omega = 0$, $\omega \sim 3$, and

$\omega \sim 4$ regions as x_1 increases and a decrease in the $\omega \sim 2$ region. Figures (9.1) through (10.4) also show the transition locus for a simple fluid square-well for comparison.

Figures (11.1) and (11.2) show the transition loci for the case N = 2, R = 1, H = 1.5, and x_1 = .5 in the (p, T) and (ρ, T) planes respectively. From the figure we can see that increasing the ratio of the well depths has increased the region of monotonic decay.

Figure (12) shows a plot of peak pressure reached by the transition loci versus concentration for the cases N = 2, R = 1, and H = 1 and 1.5. For all concentrations the peak pressure is increased as the well depth ratio is increased. This effect, an increase in the region of monotonic decay with an increase in the attractive part of the intermolecular pair potential, has been noted in previous work[1,3,13] on the effect that the attractive part of the pair potential has on the asymptotic behavior of the pair correlation function.

Our choice for the mixed interaction parameters of the pair potential does not favor any phase separation. Figure (13) shows a comparison of the transition locus with the van der Waal's spinodal for an equivalent van der Wall's mixture. The lines do not cross, and only at very low concentrations is the transition locus even close to the region of phase separation.

Figure (14) shows a plot of the transition loci in the (T, x_1) plane at constant ρ for the cases N = 2, R = 1, and H = 1 and 1.5. We note here that our plots are not a two dimensional projection from the four dimensional variable space ρ, p, T, x_1. Rather, only one variable is held constant in each plot and the fourth is given by the equation of state.

van der WAAL's SPINODAL

The free energy of a binary van der Waal's mixture is given by [12]

$$f(x,T,v) = kT(x_1nx + (1-x)\ln(1-x)) - a(x)/v - kT\ln(v-b(x)) + xh_1(T) + (1-x)h_2(T) \quad . \tag{6.31}$$

The equation for the spinodal is obtained from the solution of

$$f_{xx}f_{vv} - f_{xv}^2 = 0 \quad , \tag{6.32}$$

where the subscripts refer to the various derivatives of the free energy. The derivatives are given by

$$f_v = a(x)/v^2 - kT/(v-b(x)) \quad , \tag{6.33}$$

$$f_{vv} = -2a(x)/v^3 + kT/(v-b(x))^2 \quad , \tag{6.34}$$

$$f_x = kT(\ln x - \ln(1-x)) - a'(x)/v + kTb'(x)/(v-b) \quad , \tag{6.35}$$

$$f_{xv} = a'(x)/v^2 = kTb'(x)/(v-b(x))^2 \quad , \tag{6.36}$$

and

$$f_{xx} = kT(1/x - 1/(1-x)) - a''(x)/v + kTb''(x)/(v-b) + kT(b'(x))^2/(v-b(x))^2 \quad . \tag{6.37}$$

We now note that for a one-dimensional van der Wall's system a(x) and b(x) are given by

$$a(x) = a_1x^2 + 2a_{12}x(1-x) + a_2(1-x)^2 \quad , \tag{6.38}$$

and

$$b(x) = b_1x + b_2(1-x) \quad . \tag{6.39}$$

If we now let $\beta = 1/kT$ and substitute equations (6.34) through (6.37) into equation (6.32) we have

$$(v(v-b(x))^2 - x(1-x)((v-b(x))^2 \beta a''(x) + v(b'(x))^2))*$$
$$(-2a(x)\beta(v-b(x))^2 + v^3)/(x(1-x)v(v-b(x))^2 v^3 (v-b(x))^2)$$
$$-((v-b(x))^2 \beta a'(x) - v^2 b'(x))^2/(v^4(v-b(x))^4) = 0 \quad . \tag{6.40}$$

Multiplying out and collecting terms to the various orders in β we have the following: to order zero

$$v^4(v-b)^2 \tag{6.41}$$

the linear term

$$-2v(v-b)^2(a(x)(v-b)^2 + x(1-x)(a''(x)v^2/2 - a'(x)b'(x)v\ a(x)b'(x)^2)) \quad , \tag{6.42}$$

and the quadratic term

$$x(1-x)(v-b)^4(2a(x)a''(x) - (a'(x))^2) \quad . \tag{6.43}$$

Now for the mixtures we are dealing with $b_2 = Nb_1$, $a_2 = Ha_1$, and $a_{12} = H^{1/2} a_1$. Using these relations in equations (6.41) through (6.43) and letting $N = 2$, $H = 1$, one obtains

$$T_s = 2\rho((1-2\rho)^2 + \rho\ x_1(2-3\rho)) \quad , \tag{6.44}$$

where T_s is in units of ϵ/k, x_1 is the concentration of type 1 particles, and ρ is the normalized number density.

Phase separation is favored if $a_{12} << (a_1 + a_2)/2$ and $b_{12} >> (b_1 + b_2)/2$. This is not the case for the model mixtures we are dealing with since for our systems

$$b_{12} = (b_1 + b_2)/2 \ , \tag{6.45}$$

and
$$a_{12} = (a_1 a_2)^{1/2} \tag{6.46}$$

Recall the general form for the equation of state of a one-dimensional binary mixture equation (2.2)

$$-\rho^{-1} = x_1 J_{11}'(\xi)/J_{11}(\xi) + x_2 J_{22}'(\xi)/J_{22}(\xi) + \frac{\partial C}{\partial \xi} \quad . \tag{2.2}$$

For our square-well model mixtures the Boltzmann factors are given by

$$J_{11}(u) = be^{v-u} A1/u \quad , \tag{7.1}$$

$$J_{11}'(u) = b^2 e^{v-u}(A2 - A1 - A1/u)/u \quad , \tag{7.2}$$

$$J_{22}(u) = be^{Hv-Nu} B1/u \quad , \tag{7.3}$$

$$J_{22}'(u) = b^2 e^{Hv-Nu}(B2 - Nb1 - B1/u)/u \quad , \tag{7.4}$$

where

$$A1 = A_{11} \quad , \tag{7.5}$$

$$A2 = Re^{-Ru} - Re^{-Ru-v} \quad , \tag{7.6}$$

$$B1 = B_{11} \quad , \tag{7.7}$$

and
$$B2 = RNe^{-RNu} - RNe^{-RNu-Hv} \quad . \tag{7.8}$$

If we now let

$$C1 = A_{12} \tag{7.9}$$

and
$$C2 = CRe^{-CRu} - CRe^{-CRu-H^{1/2}v} \quad , \tag{7.10}$$

we have for our equation of state

$$(b\rho)^{-1} = x_1(B2/B1 - N - A2/A1) - B2/B1 + (N + u)/u$$
$$+ D(x_1/(\Gamma - 1 + 2x_1) + x_2/(\Gamma + 1 - 2x_1) - 1/(\Gamma + 1) \quad , \tag{7.11}$$

where

$$D = \frac{2x_1x_2(e^{V}A1B2/C1^{2} + e^{V}B1A2/C1^{2} - 2e^{V}A1B1C2/C1^{3})}{(1 + 4x_1x_2(e^{V}A1B1/C1^{2} - 1))^{1/2}} \tag{7.12}$$

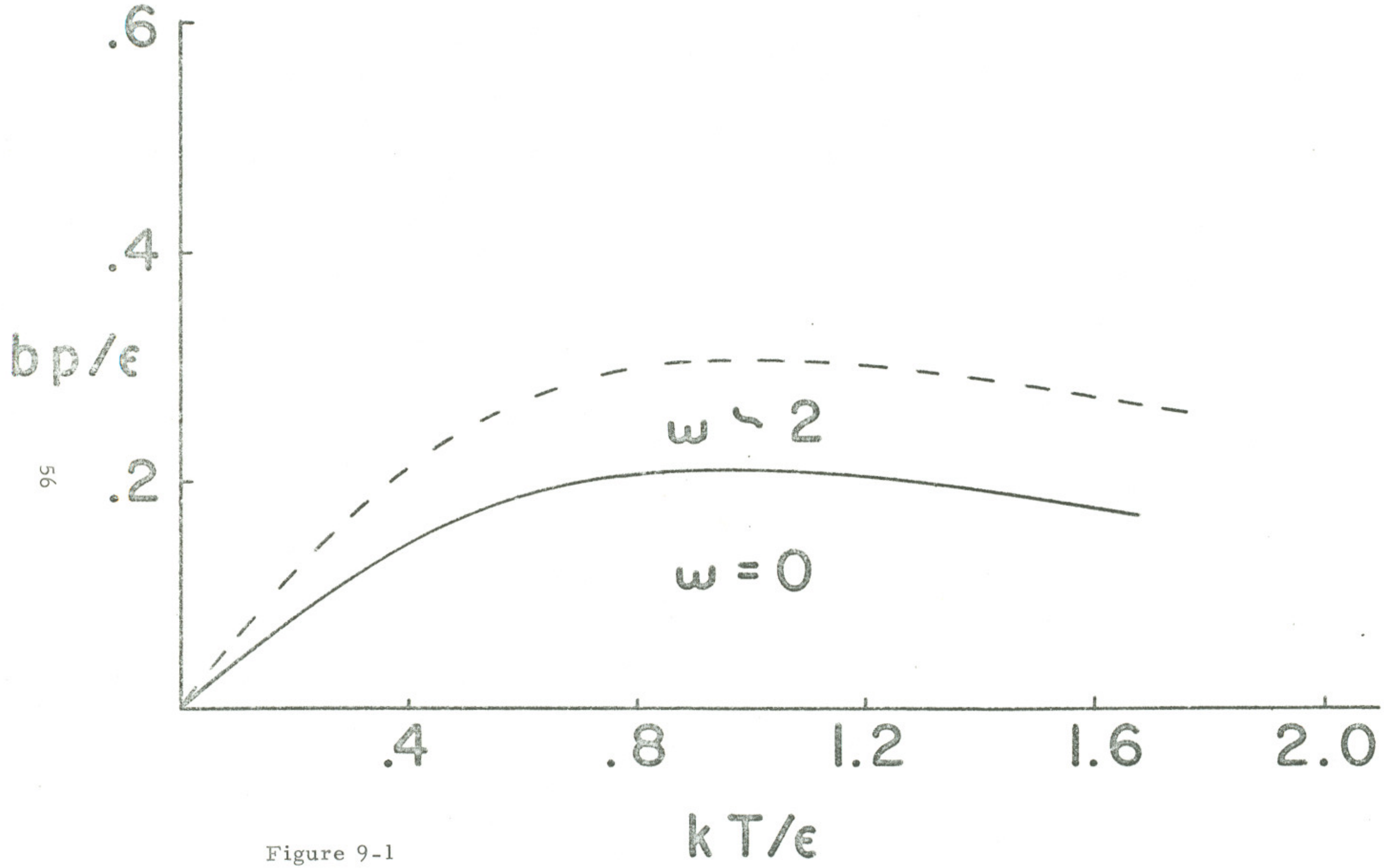


Figure 9-1

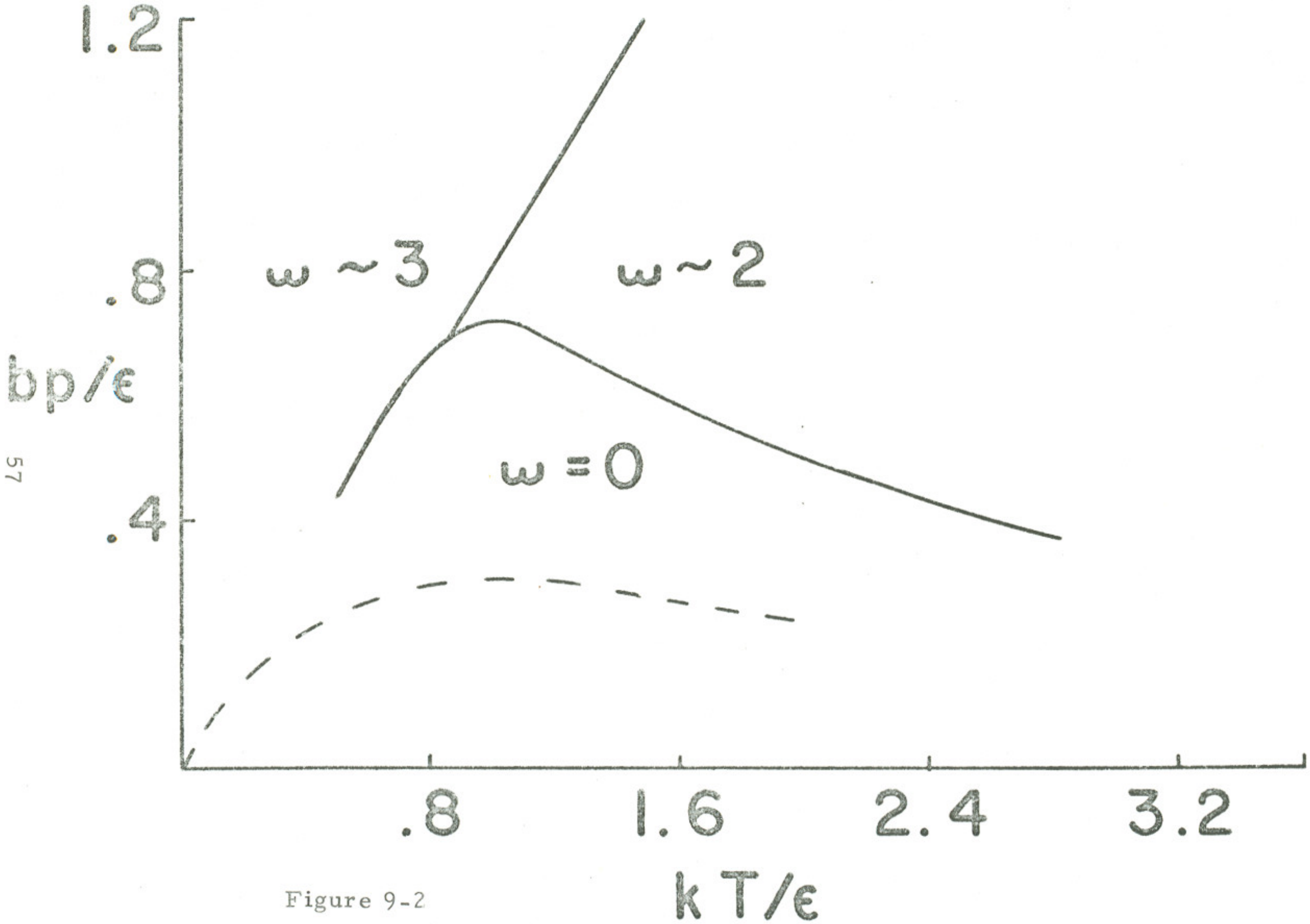
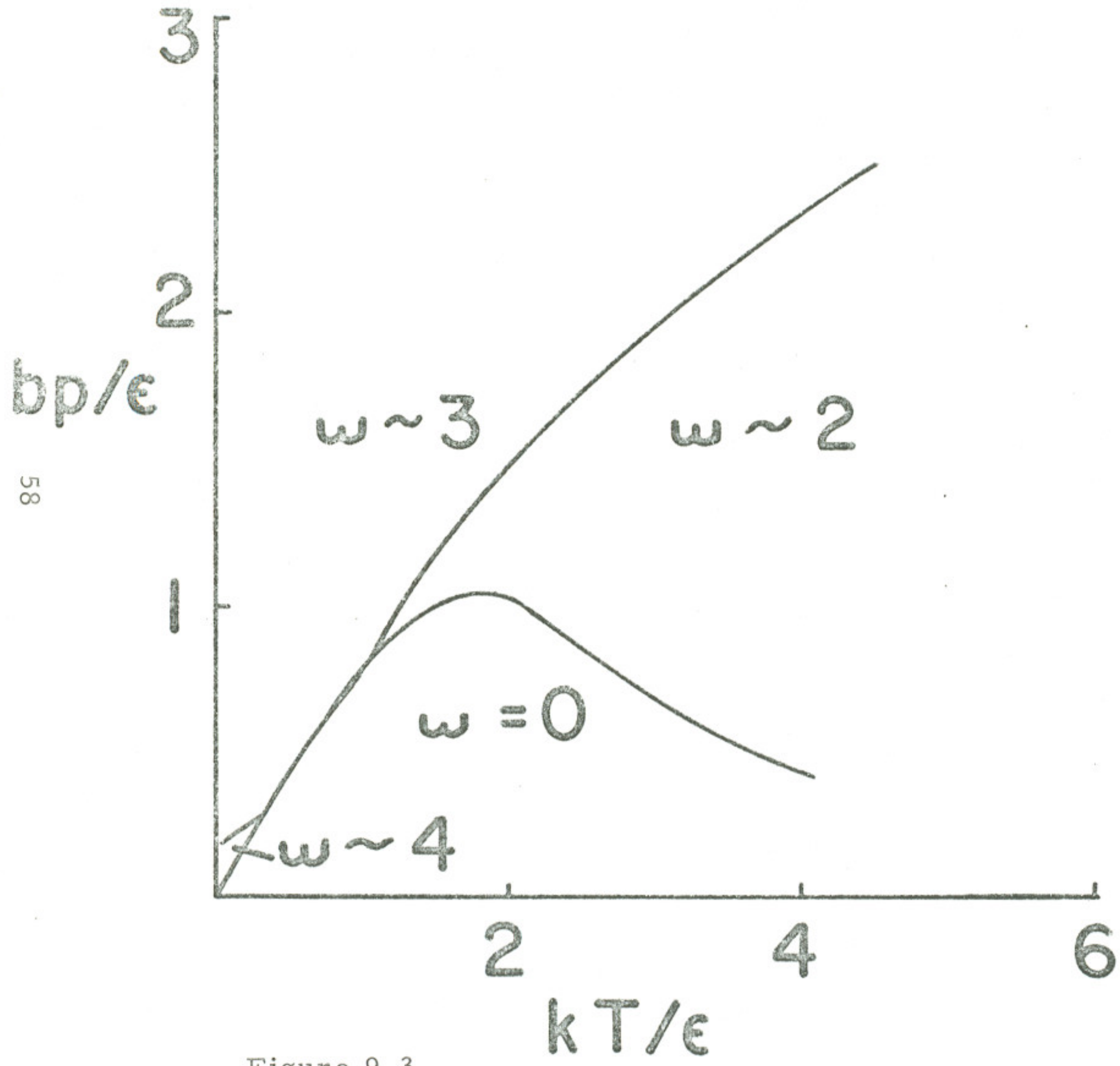


Figure 9-2



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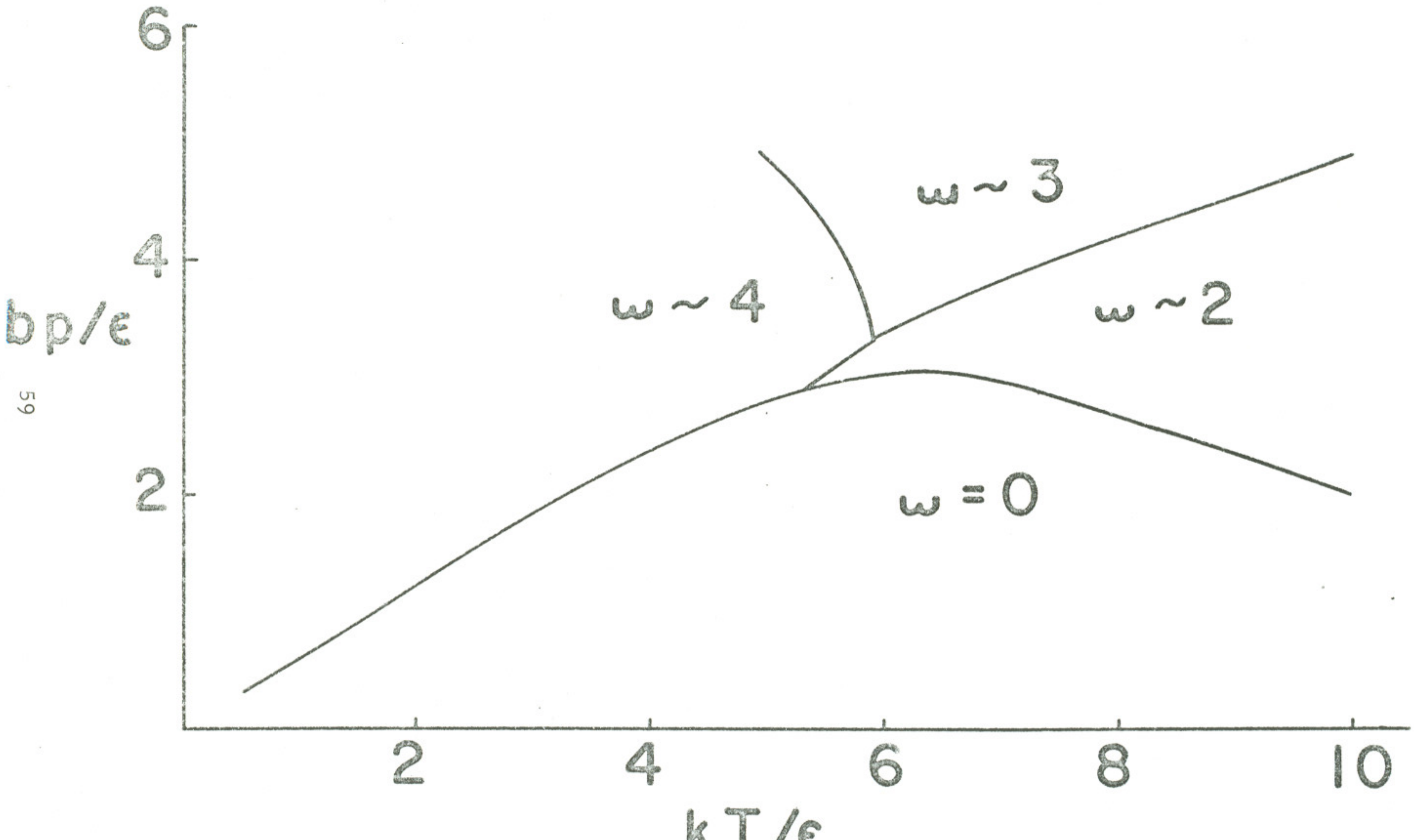

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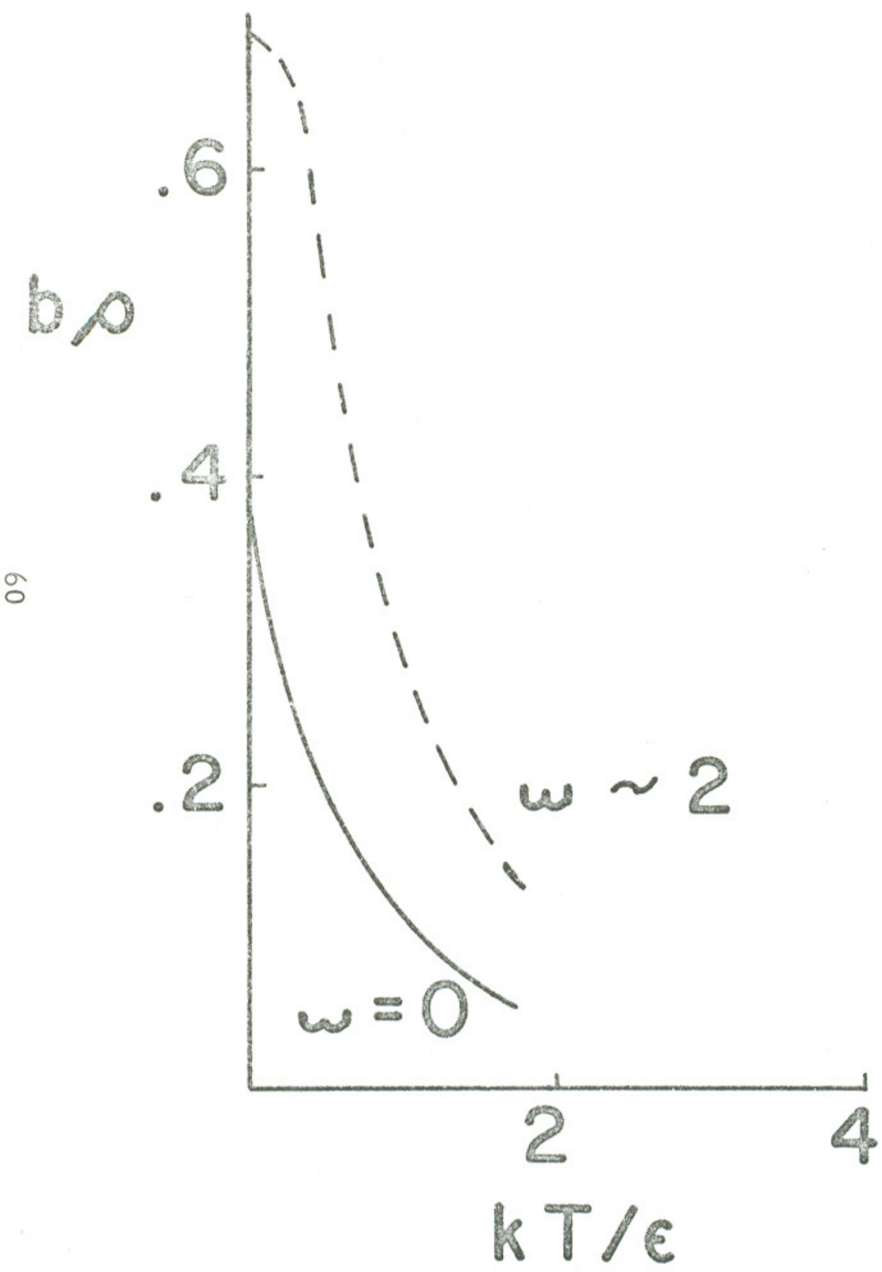


Figure 10-1

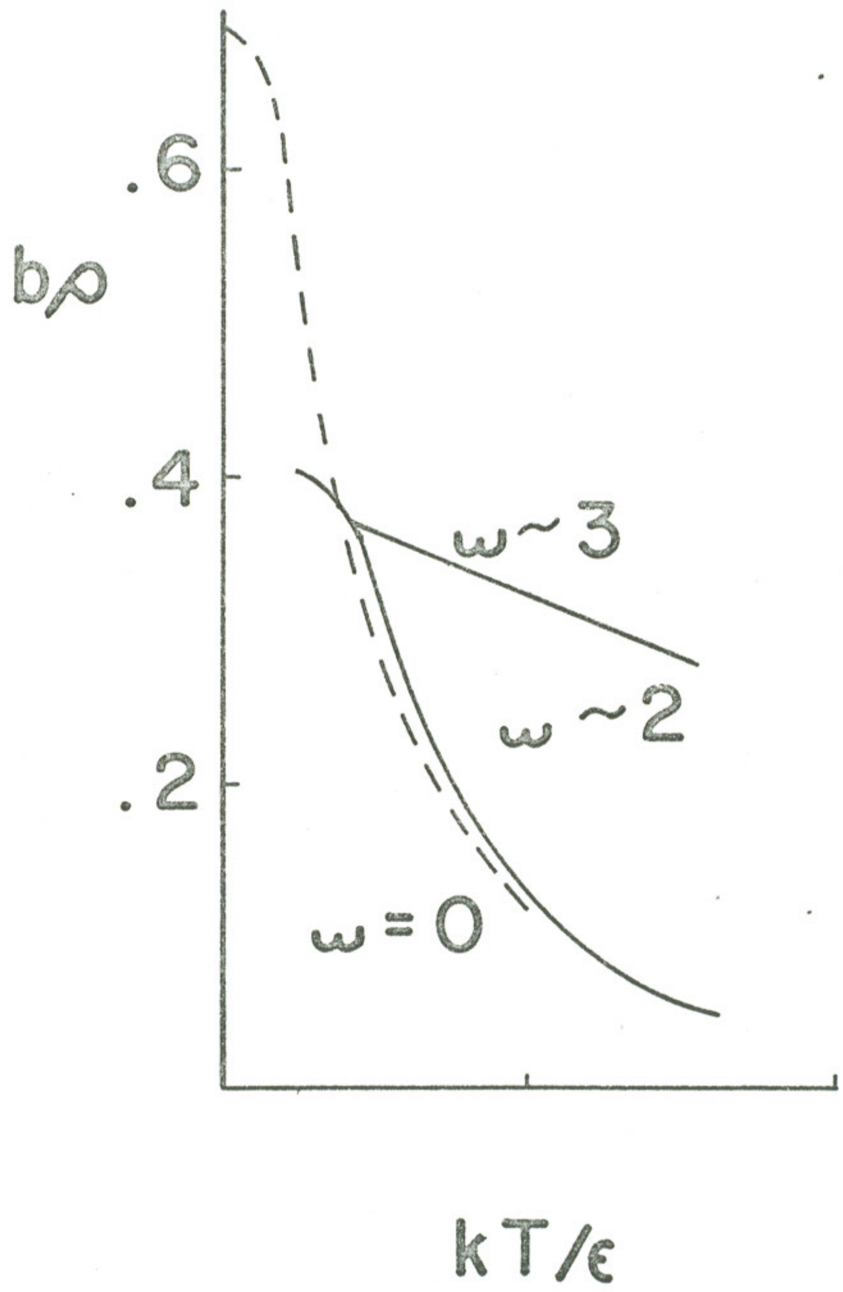


Figure 10-2

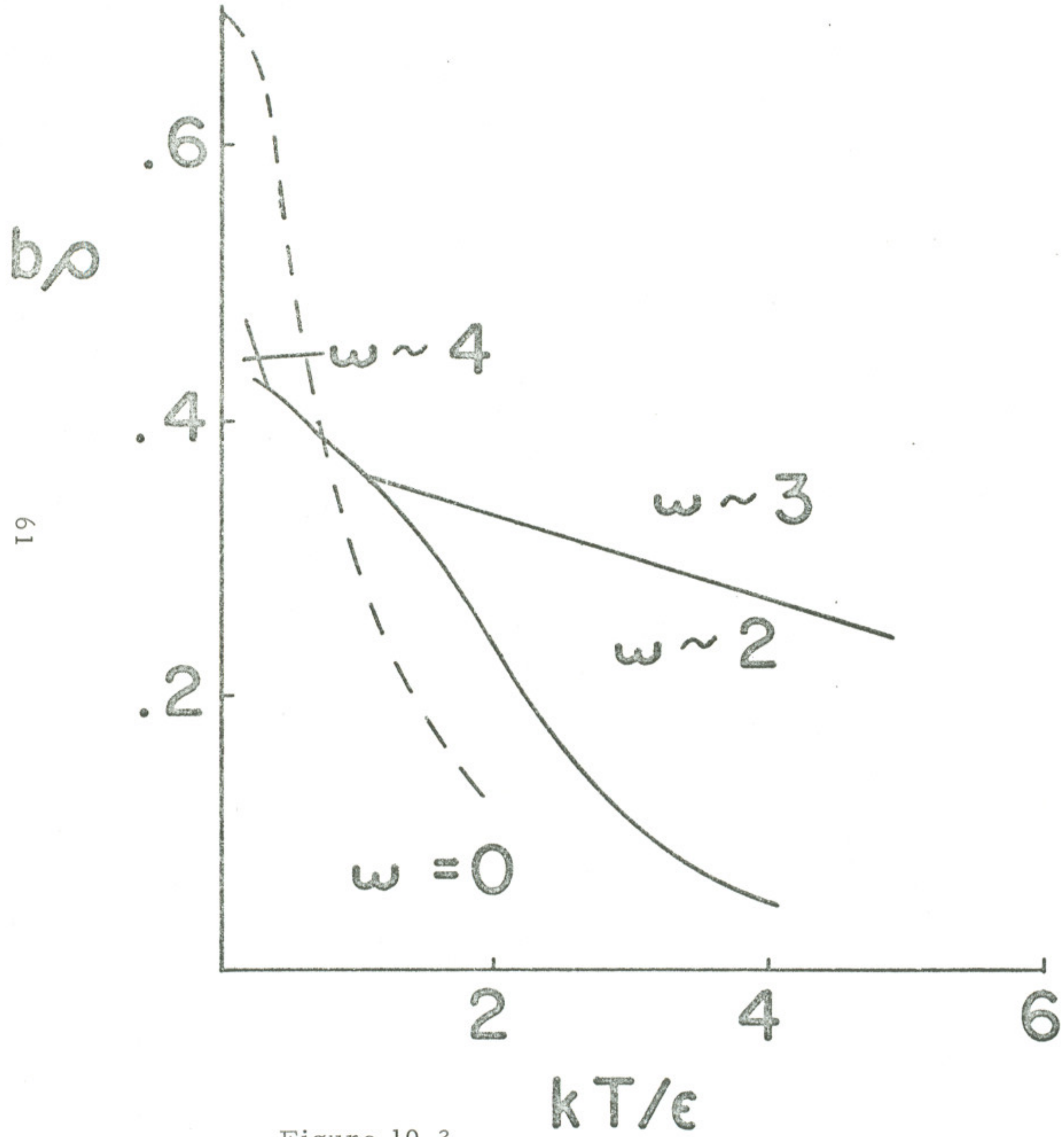


Figure 10-3

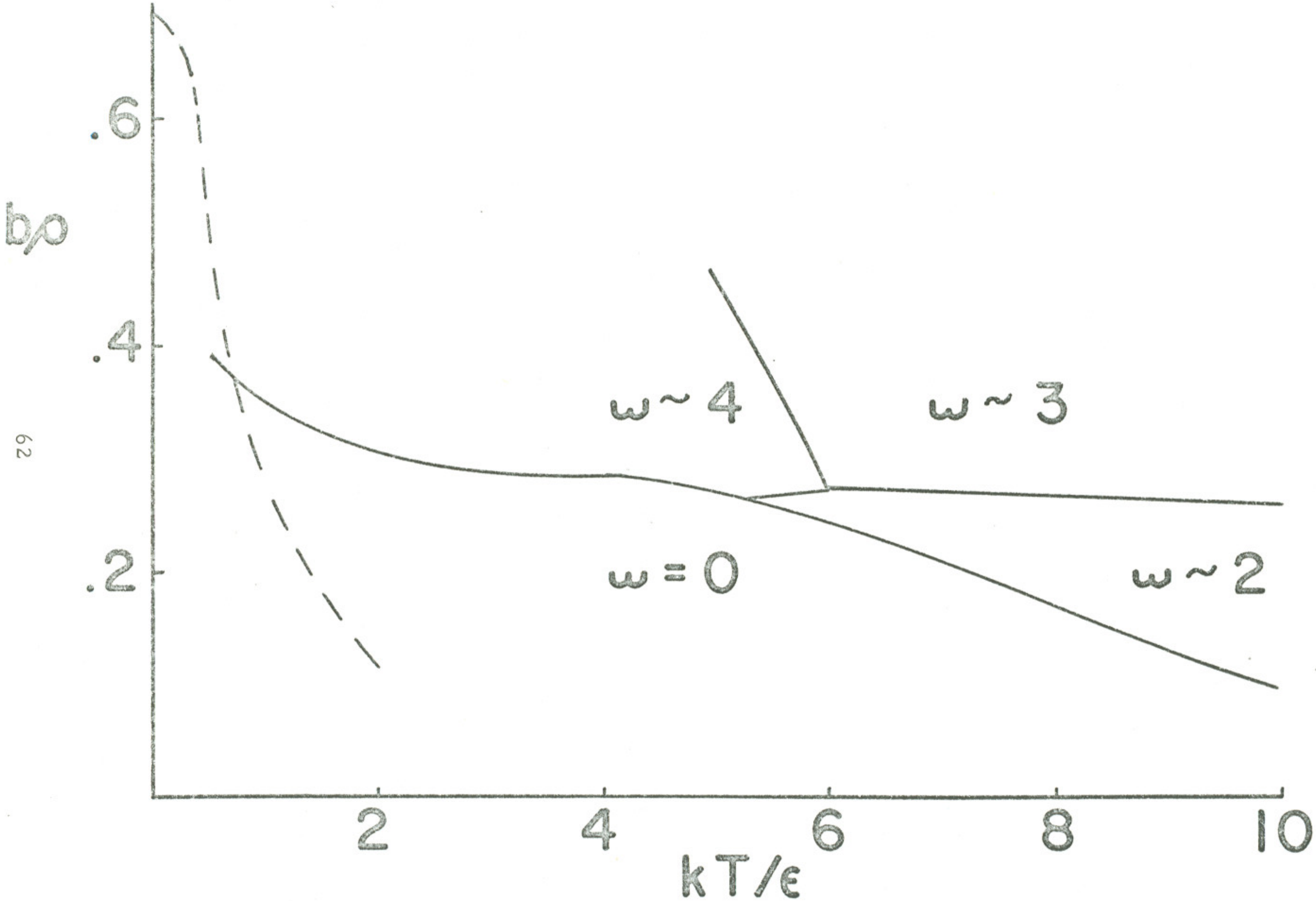


Figure 10-4

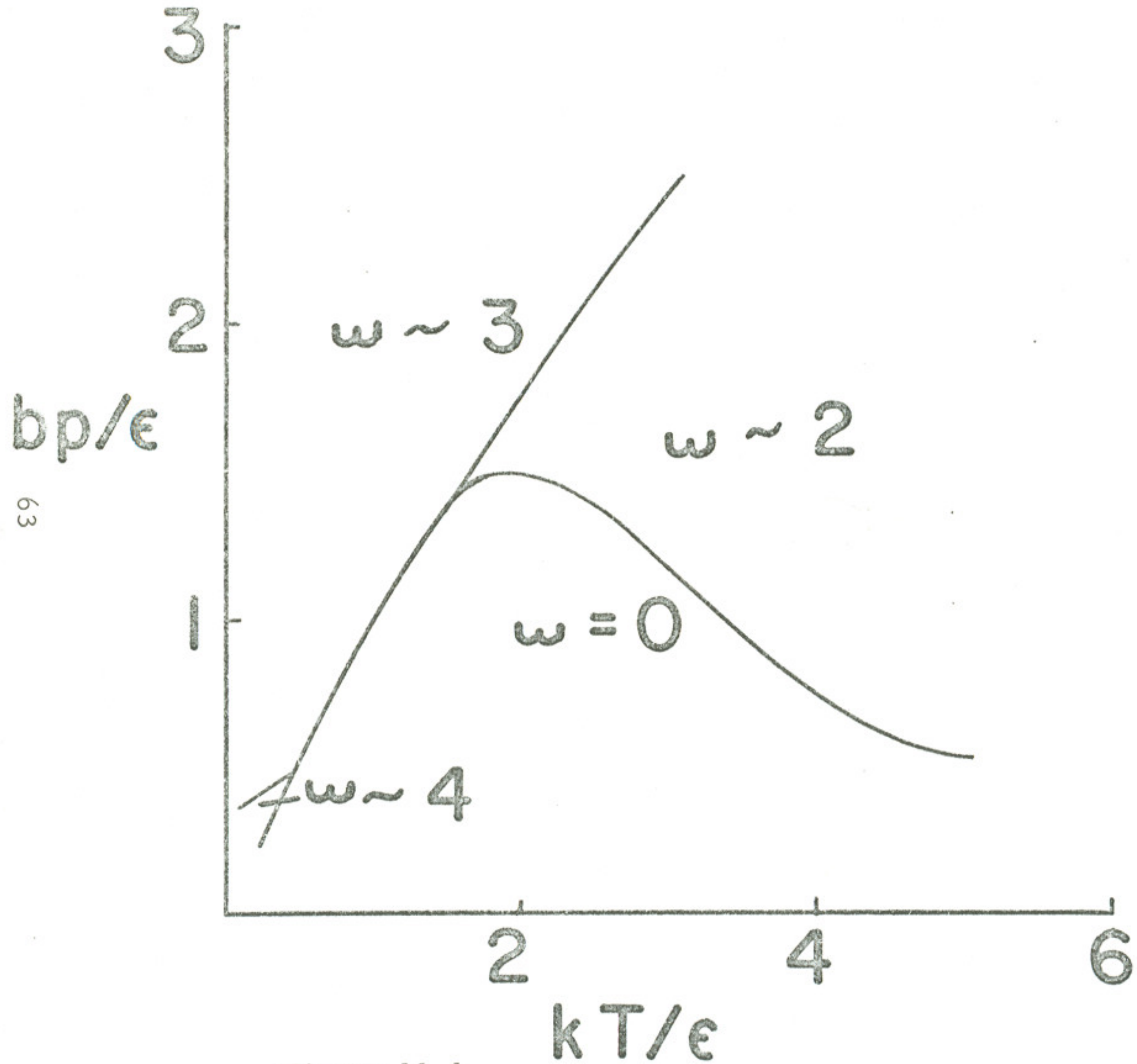


Figure 11-1

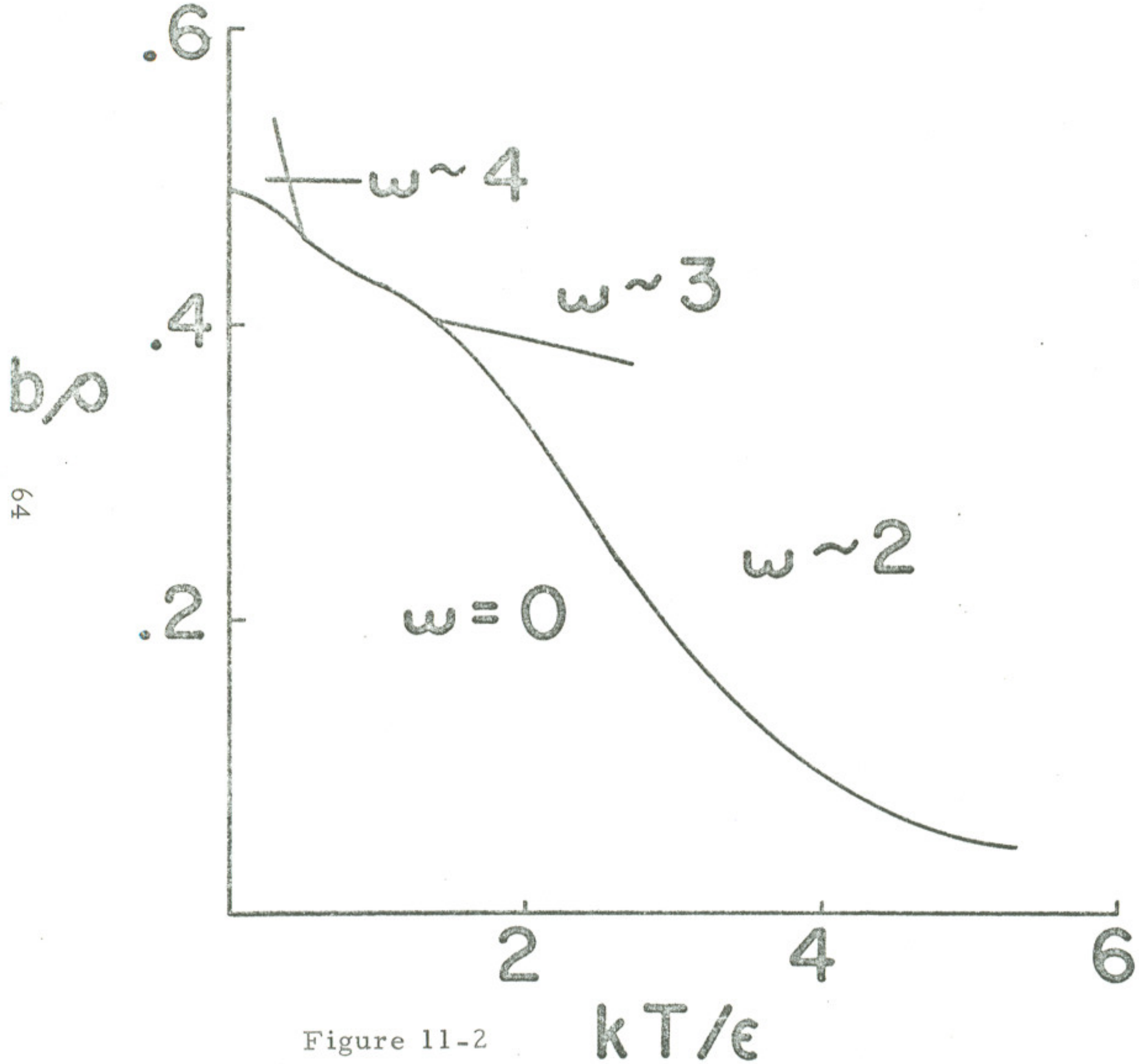


Figure 11-2

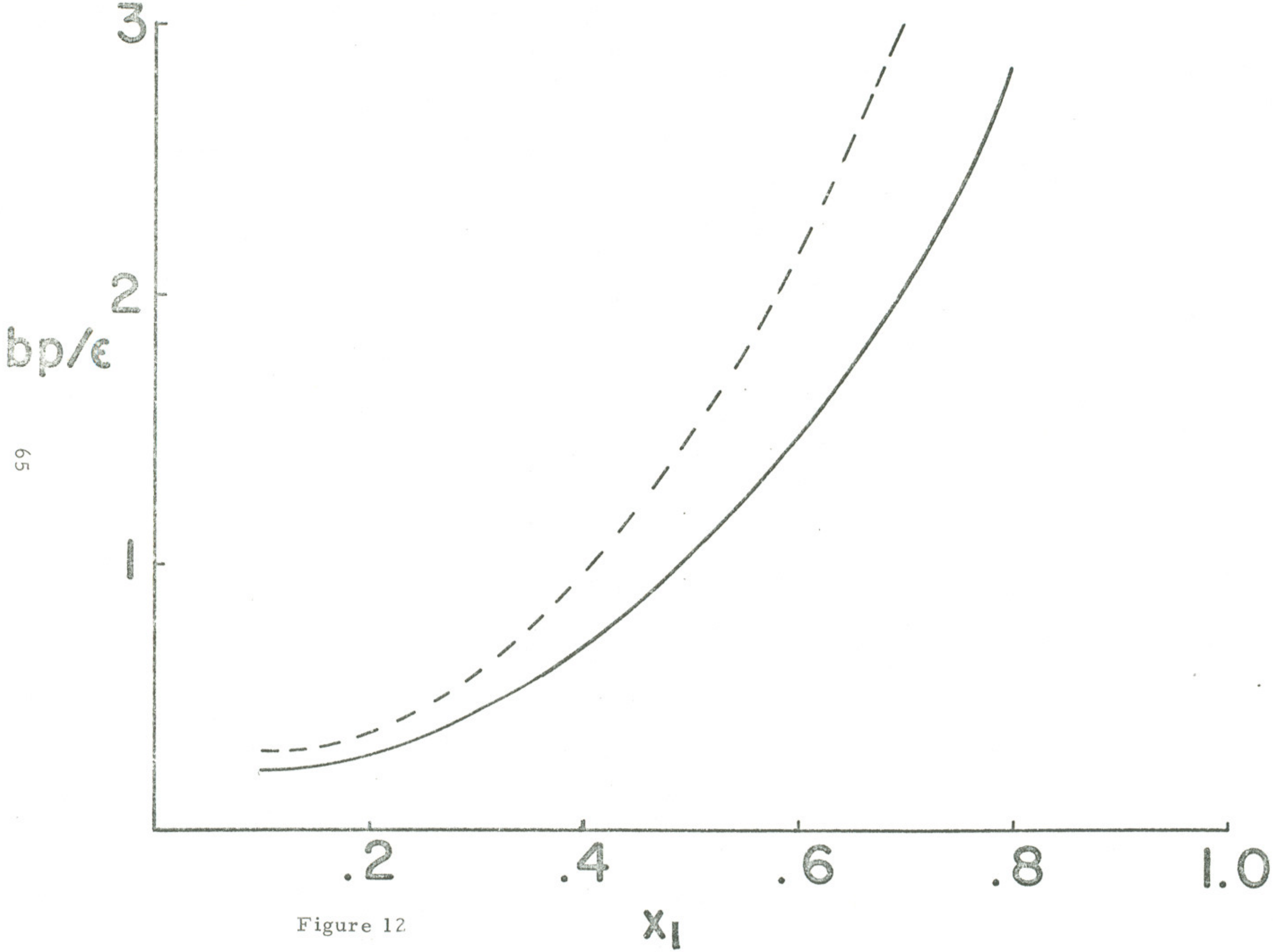


Figure 12

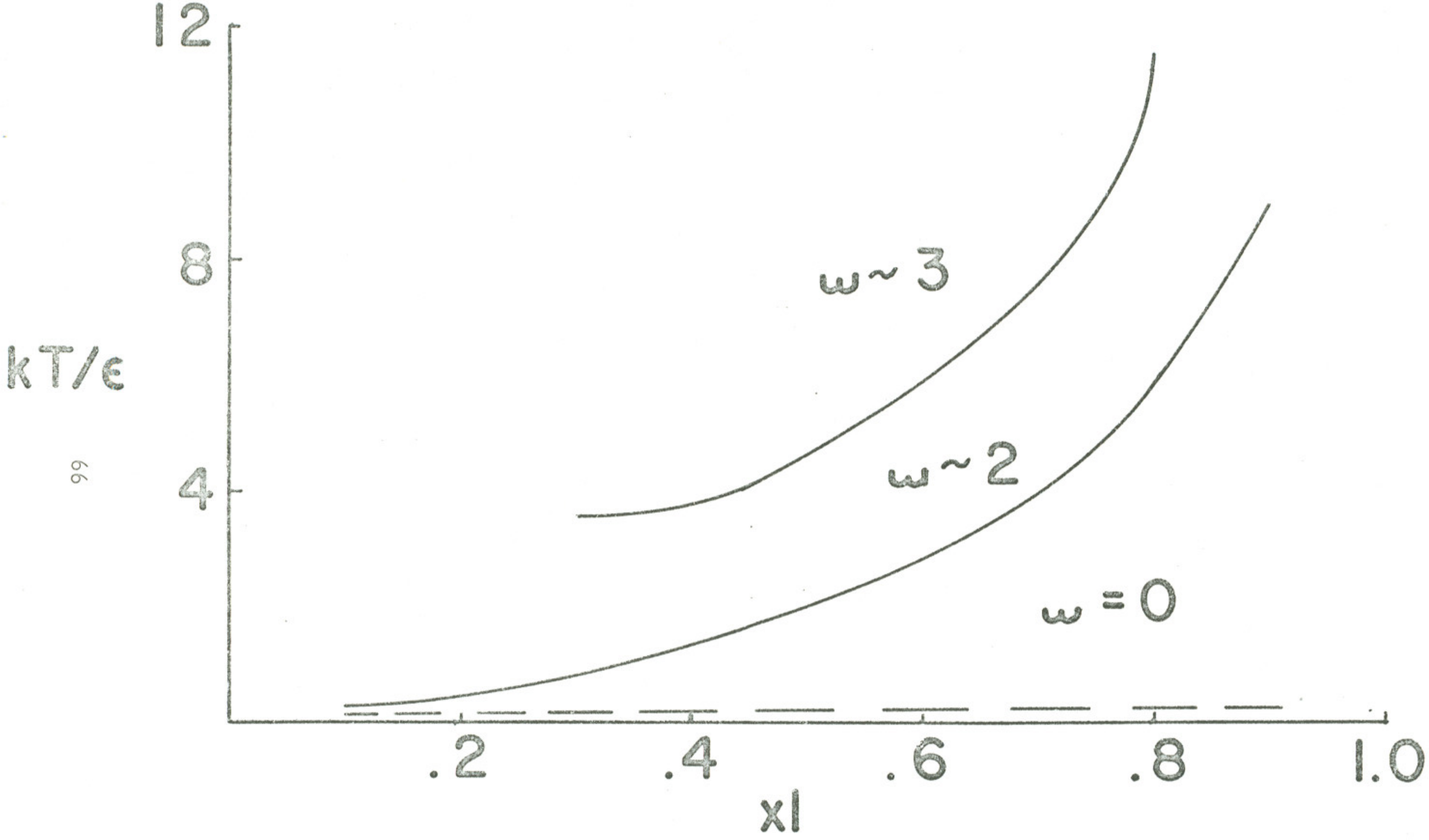


Figure 13

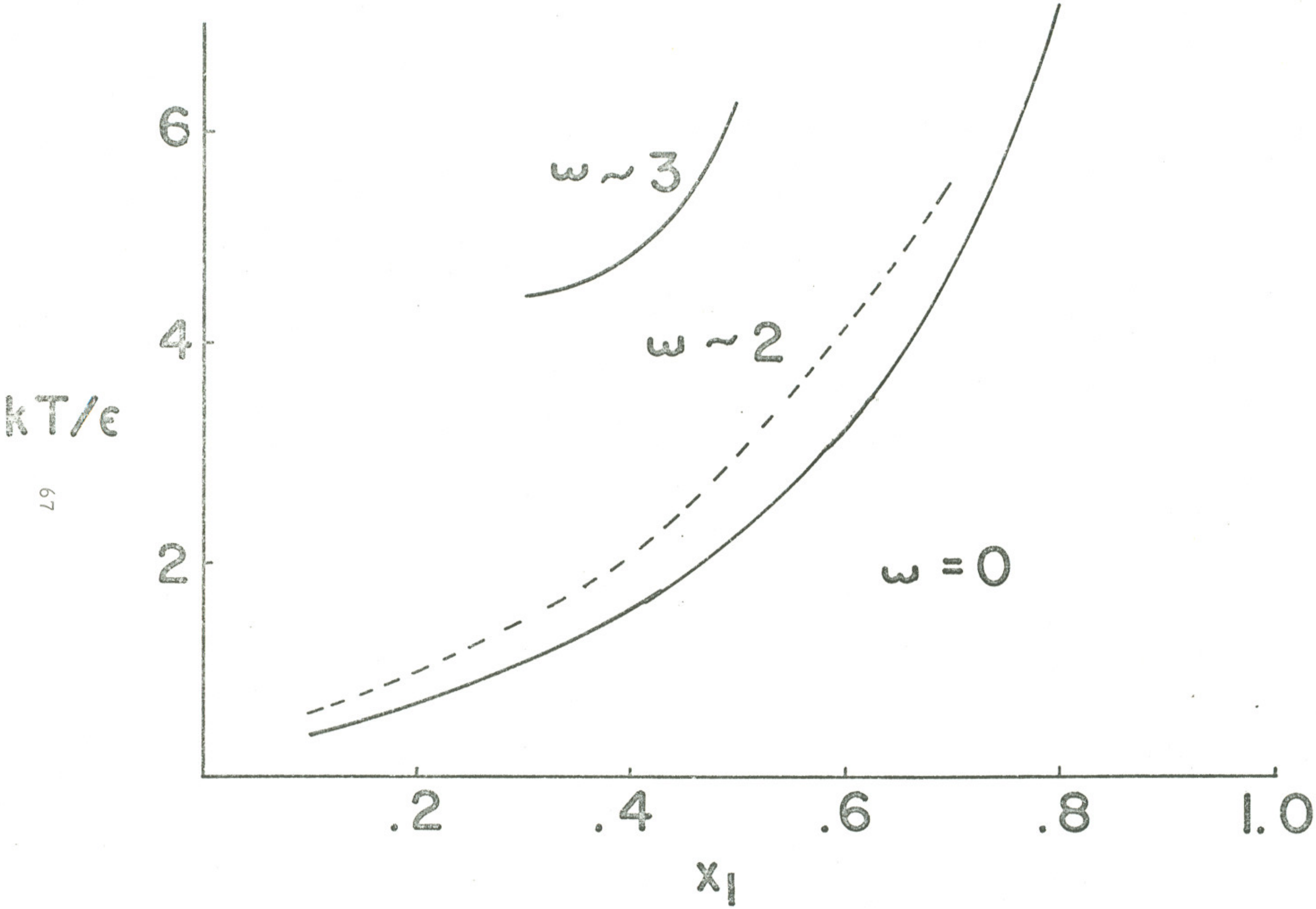


Figure 14

LATTICE GAS HARD SPHERES

In going from the linear continuum to the lattice gas we use the following prescription:

$$\int_0^{\infty} dr \rightarrow a \sum_{k=0}^{\infty} (r \rightarrow ka) \, . \tag{5.1}$$

Thus

$$J_{ij}(s) = a \sum_{k=0}^{\infty} e^{-ska} e^{-\beta\phi_{ij}(ka)} \quad . \tag{5.2}$$

Let $\phi_{ij}(r)$ be given by

$$\begin{aligned} \phi_{ij}(r) &= \infty \, , \; r < b_{ij} \\ &= 0 \, , \; 4 \geq b_{ij} \quad , \end{aligned} \tag{5.3}$$

and furthermore let

$$\begin{aligned} b_{11} &= b \\ b_{22} &= Nb \\ B_{12} &= ((N+1)/2)b = Cb \end{aligned}$$

and

$$b = Ma$$

where a is the lattice constant and b is the hard sphere diameter of the smaller species. Then

$$J_{11}(\xi) = a \sum_{k=0}^{\infty} e^{-\xi ka} e^{-\beta\phi_{11}(ka)}$$

$$= a\left(\sum_{k=0}^{M-1} e^{-\xi ka} e^{-\beta\phi_{11}(ka)} + \sum_{k=M}^{\infty} e^{-\xi ka - \beta\phi_{11}(ka)} \right)$$

$$= a(0 + e^{-M\xi a}/(1-e^{-\xi a}))$$

$$= ae^{-Mu}/(1-e^{-u}) \quad , u = \xi a \ , \tag{5.4}$$

$$J_{11}(\xi + s) = ae^{-M(u+\ \ )}/(1-e^{-(u+\lambda)}) \ , \lambda = as \ , \tag{5.5}$$

$$J_{22}(\xi) = a \sum_{k=0}^{oo} e^{-\xi ka - \beta\phi_{22}(ka)}$$

$$= a(\sum_{k=0}^{NM-1} e^{-\xi ka - \beta\phi_{22}(ka)} + \sum_{k=NM}^{oo} e^{-\xi ka - \beta\phi_{22}(ka)})$$

$$= a(0 + e^{-NMa\xi}/(1-e^{-a\xi}))$$

$$= ae^{-MNu}/(1-e^{-u}) \quad , \tag{5.6}$$

$$J_{22}(\xi+s) = ae^{-MN(u+\lambda)}/(1-e^{-(u+\lambda)}) \quad , \tag{5.7}$$

$$J_{12}(\xi) = ae^{-MCu}/(1-e^{-u}) \quad , \tag{5.8}$$

and
$$J_{12}(\xi+s) = ae^{-Mc(u+\lambda)}/(1-e^{-(u+\lambda)}) \quad . \tag{5.9}$$

Now for the moment let M = 2. Substituting equations (5.5-5.9) into the expressions for the P_{ij}'s and remembering that $\Gamma = 1$ for hard-spheres, we have

$$P_{11} = x_1(1-e^{-u})e^{-2\lambda}/(1-e^{-(u+\lambda)}) \quad , \tag{5.10}$$

$$P_{22} = x_2(1-e^{-u})e^{-2N\lambda}/(1-e^{-(u+\lambda)}) \quad , \tag{5.11}$$

$$P_{12} = x_2(1-e^{-u})e^{-(N+1)\lambda}/(1-e^{-(u+\lambda)}) \quad , \tag{5.12}$$

and
$$P_{21} = x_1(1-e^{-u})e^{-(N+1)\lambda}/(1-e^{-(u+\lambda)}) \quad , \tag{5.13}$$

From equation (5.12) and equation (5.13) we can see that $P_{11}P_{22} = P_{12}P_{21}$, so that our equation reduces to

$$x_1(1-e^{-u})e^{-2\lambda}/(1-e^{-(u+\lambda)}) + x_2(1-e^{-u})e^{-2N\lambda}/(1-e^{-(u+\lambda)}) = 1 ,$$

or
$$e^{2N\lambda} - e^{-u}e^{-\lambda(1-2N)} - x_1(1-3^{-u})e^{2\lambda(N-1)}$$
$$-(1-x_1)(1-e^{-u}) = 0 \quad . \qquad (5.14)$$

We know that $\lambda = 0$ is the trivial root and so we divide it out. We then have

$$z^{2N-1} + Az^{2N-2} + ABz^{2N-3} + \ldots + AB = 0 , \qquad (5.15)$$

where
$$z = e^{\lambda} ,$$
$$A = 1-e^{-u} ,$$
$$B = 1-x_1 .$$

Therefore, when 2N is integral, the equation governing the asymptotic behavior of the pair correlation function is a polynomial of degree 2N-1, where N is the ratio of the hard sphere diameters. Since all the coefficients of equation (5.15) are positive, the roots will either be negative, or complex conjugate pairs.

Let $z = z_o'$, where z_o' is a root of equation (5.15). Then if z_o' is real and negative

$$e^{\lambda} = z_o' = -z_o$$
$$e^{x}(\cos y + i \sin y) = -z_o$$
$$e^{x}\cos y = -z_o$$

$$e^x \sin y = 0$$

$$y = k\pi \quad , k = 0,1,2,3,\ldots \quad ,$$

$$e^x \cos(k\pi) = -z_o$$

$$e^x = z_o$$

$$x = \ln z_o \; , k = 1,3,5,\ldots \quad ,$$

since x is real.

So, for z_o' real and negative

$$\lambda = \ln z_o + ik\pi \quad , \quad k = 1,3,5, \ldots \quad . \tag{5.16}$$

For z_o' complex we let $z_o' = x_o + iy_o$, then

$$e^x(\cos y + i\sin y) = x_o + iy_o \quad ,$$

$$e^x \cos y = x_o$$

$$e^x \sin y = y_o$$

$$\tan y = y_o/x_o$$

$$y = \operatorname{atn}(y_o/x_o)$$

$$x = \ln(xo/\cos y) \quad ,$$

and thus

$$\lambda = \ln(x_o) - \ln[\cos(\operatorname{atn}(y_o/x_o)] + i \operatorname{atn} y_o/x_o \quad . \tag{5.17}$$

Therefore for all allowable values of z, λ is complex and thus the asymptotic decay of G(r) will always be oscillatory. However, the form of λ changes depending upon whether z_o' is real and negative or complex. When the real root is equal to the real part of the complex root, then a locus is generated in the (u,x_1) plane across which the asymptotic form of the pair correlation function abruptly changes its spatial frequency.

For any value of M equation (5.15) becomes

$$z^{MN-1} + Az^{MN-2} + ABz^{MN-3} + \ldots + AB = 0 \quad , \qquad (5.18)$$

where again

$$z = e^{\lambda}$$

$$A = 1-e^{-u}$$

and

$$B = 1-x_1 \quad .$$

Let us now consider some specific cases.

Case 1.) N = 1, M = 2, simple fluid case -

$$z + A = 0 \quad ,$$

$$e^{\lambda} = e^{-u}-1$$

$$e^{x}(\cos y + i\sin y) = e^{-u}-1 \quad ,$$

$$e^{x}\cos y = e^{-u}-1 \quad ,$$

$$e^{x}\sin y = 0$$

$$y = k\pi \; ; \; k = 0,1,2,3,4,\ldots \quad .$$

So

$$e^{x}\cos k\pi = e^{-u}-1$$

$$e^{x} = e^{-u}-1, \; k = 0,2,4,\ldots \quad ,$$

$$e^{x} = 1-e^{-u}; \; k = 1,3,5,\ldots \quad .$$

Since x is real only odd k are acceptable and we have

$$\lambda = \ln(1-e^{-u}) + ik\pi \; ; \quad k = 1,3,5,\ldots \quad . \qquad (5.19)$$

Thus the form of λ remains the same over the entire range of u. (Note: This is the expected simple fluid result.) Figure 15 shows a comparison of the simple fluid case for the linear continuum and the lattice gas.

Case 2.) $N = 1.5$, $M = 2.$ -

$$z^2 + Az + AB = 0 \quad ,$$

$$z = -A/2 \pm {}^{1/2}(A^2 - 4AB)^{1/2} \quad .$$

Now let $C = A^2 - 4AB$. The form of z will then change depending upon whether C is greater than or less than zero. For $C > 0$

$$e^{\lambda} = -A/2 \pm C^{1/2}/2 \quad ,$$

or once again setting $\lambda = x + iy$

$$e^x \cos y = -A/2 \pm C^{1/2}/2 \quad ,$$

$$e^x \sin y = 0$$

$$y = k\pi \; ; \; k \; 0,1,2,3, \ldots \quad ,$$

and again because x is real and $(-A/2 \pm C^{1/2}/2)$ must be negative, only odd k are acceptable and thus

$$\lambda = \ln(A/2 + C^{1/2}/2) + ik\pi \quad ; \; k = 1,3,5, \ldots \quad .$$

For $C < 0$

$$e^{\lambda} = -A/2 \pm iC_1^{1/2}/2 \quad ; \quad C_1 = -C = i^2 C \quad ,$$

$$e^x \cos y = -A/2$$

$$e^x \sin y = \pm C_1^{1/2}/2$$

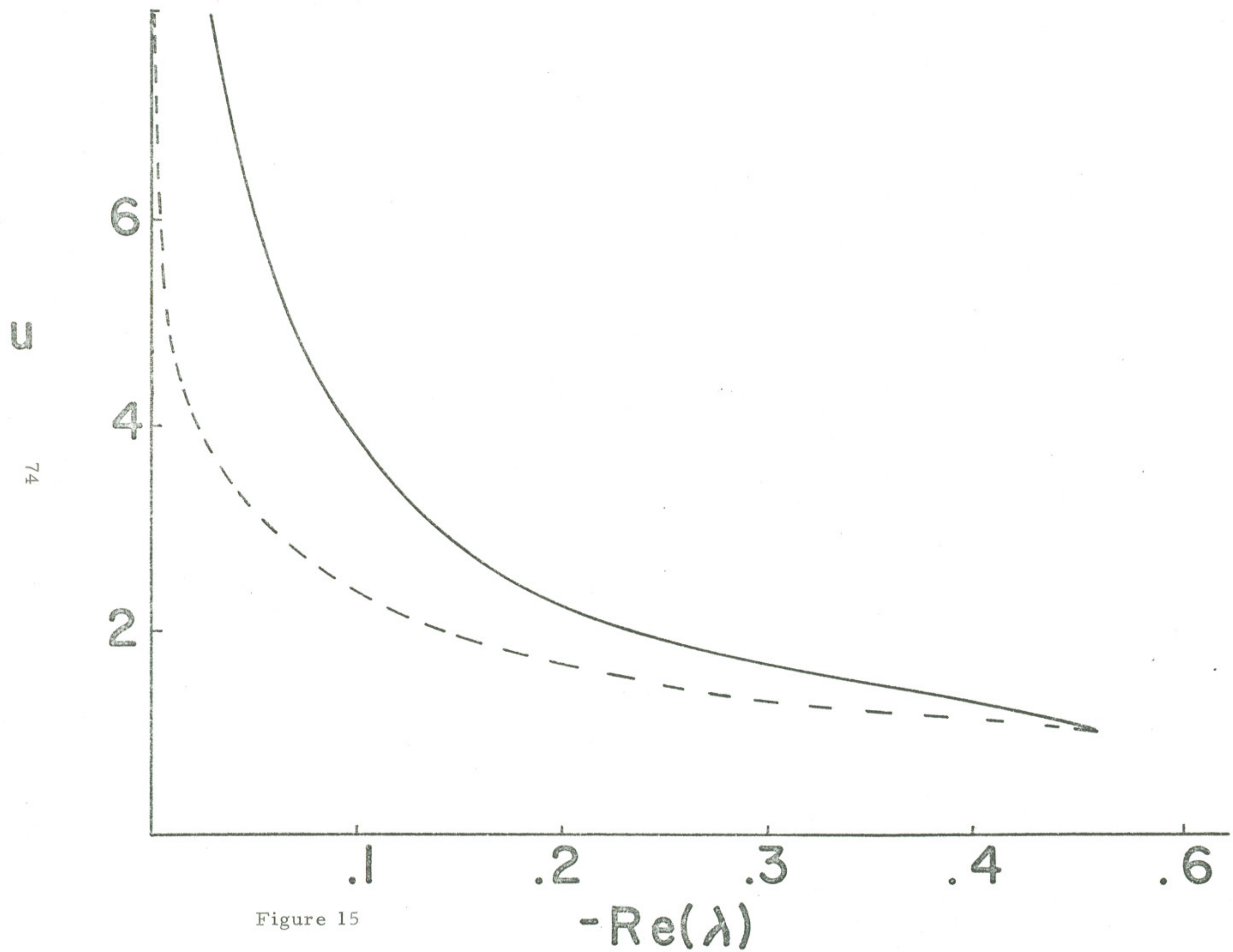


Figure 15

$$y = \text{atn}\,(\mp C_1^{1/2}/A)$$

$$x = \ln\,(-A/2\cos(\text{atn}(\mp C_1^{1/2}/A))) \quad ,$$

or

$$\lambda = \ln(-A/(2\cos(\text{atn}(+C_1^{1/2}/A)))) + i\,\text{atn}\,(+C_1^{1/2}/A). \tag{5.20}$$

The change in λ takes place when $C = 0$. Thus u_c is given by

$$A^2 - 4AB = 0$$

$$A = 4B$$

$$1-e^{-u} = 4(1-x_1)$$

$$u_c = -\ln(4x_1 - 3) \quad .$$

Therefore a locus is generated in the (u,x_1) plane across which the asymptotic decay of the pair correlation function abruptly changes its spatial frequency.

Case 3.) $N = 2$, $M = 2$, -

$$z^3 + Az^2 + ABz + AB = 0 \quad . \tag{5.21}$$

Let

$$p = A \quad , \tag{5.22}$$

$$q = AB \quad , \tag{5.23}$$

$$r = AB \quad , \tag{5.24}$$

$$a = (1/3)(3q - p^2) \quad , \tag{5.25}$$

$$b = (1/27)(2p^3 - 9pq + 27r) \quad , \tag{5.26}$$

and

$$C = a^3/27 + b^2/4 \quad . \tag{5.27}$$

Substituting equations (5.22) through (5.26) into equation (5.27) we find that $C > 0$ and thus the roots of equation (5.21) will be one real negative root and one complex pair of roots. For the real part of the complex root to equal the real root b must be equal to zero. However, this implies that $81B^2/4 - 54B > 0$. Since $B < 1$ this is impossible and thus there is no split in spatial frequency.

Case 4.) $N = 2$, $M = 1.5$ -

$$x^2 + Az + B = 0 \qquad (5.28)$$

This case will have a split in spatial frequency when $A = 4b$, or $u_c = -\ln(4x_1 - 3)$. In fact, due to the nature of the general equation, there will always be a locus generated in the (ρ, x_1) plane whenever the product MN is an odd integer. Figure (16) shows a plot of the locus in the (ρ, x_1) plane for the case $MN = 3$. Also shown is the locus for the linear continuum $N = 2$ case.

Figures (15-1) and (15-2) show plots of λ versus x_1 for both lattice gas ($MN = 3$) and linear continuum ($N = 2$) systems. The points at $x_1 = 0$ and $x_1 = 1$ are the values for 'pureB' and 'pure A' systems respectively. (See appendix D). The dashed lines in Figure (15-1) indicate the abrupt changes in $\mathrm{Im}(\lambda)$. As one can see from the figure both the lattice gas and linear continuum systems change from "low" to "high" spatial frequency as x_1 increases. Again this is the change from "B type" to "A type" behavior.

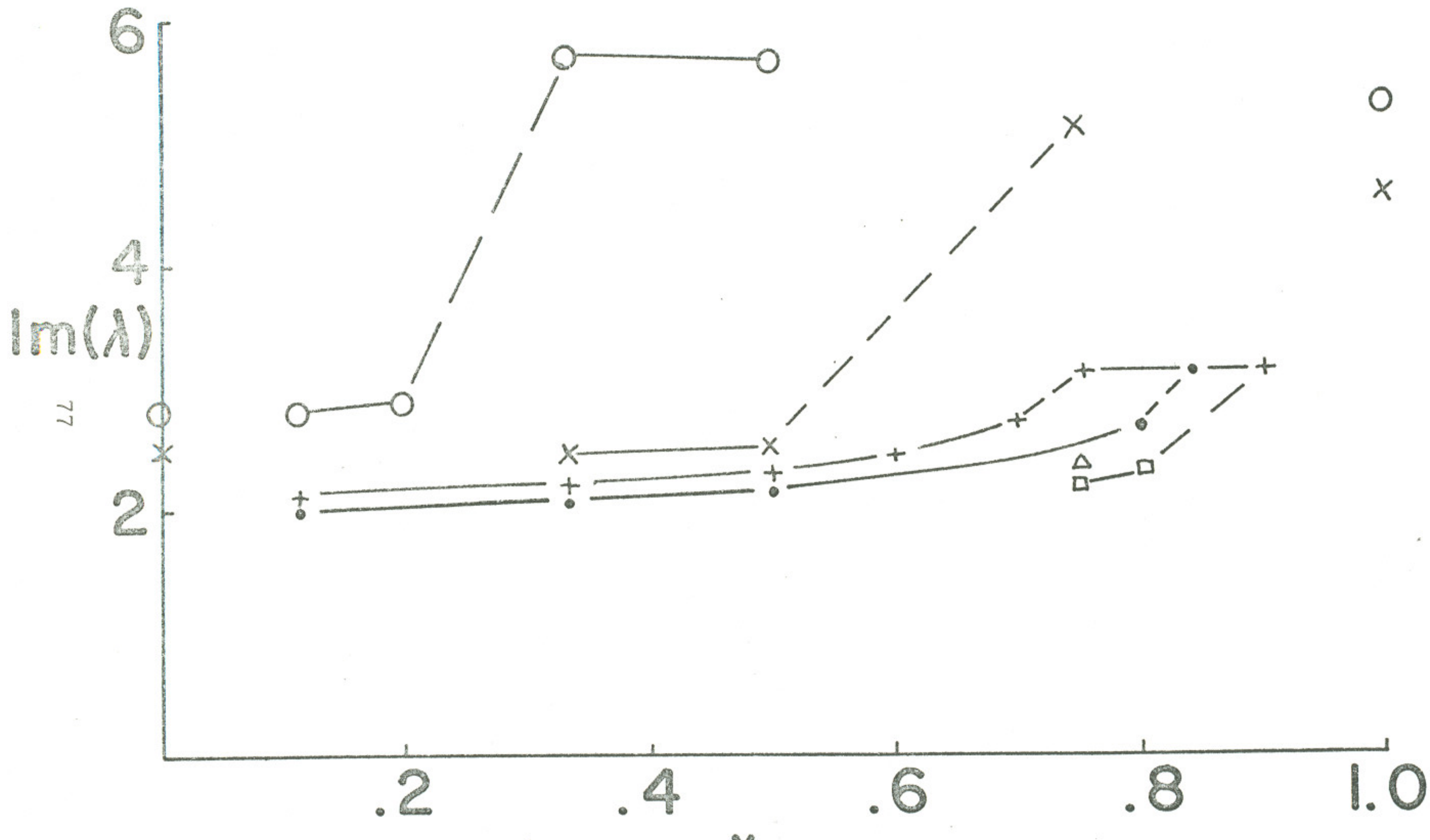


Figure 15-1

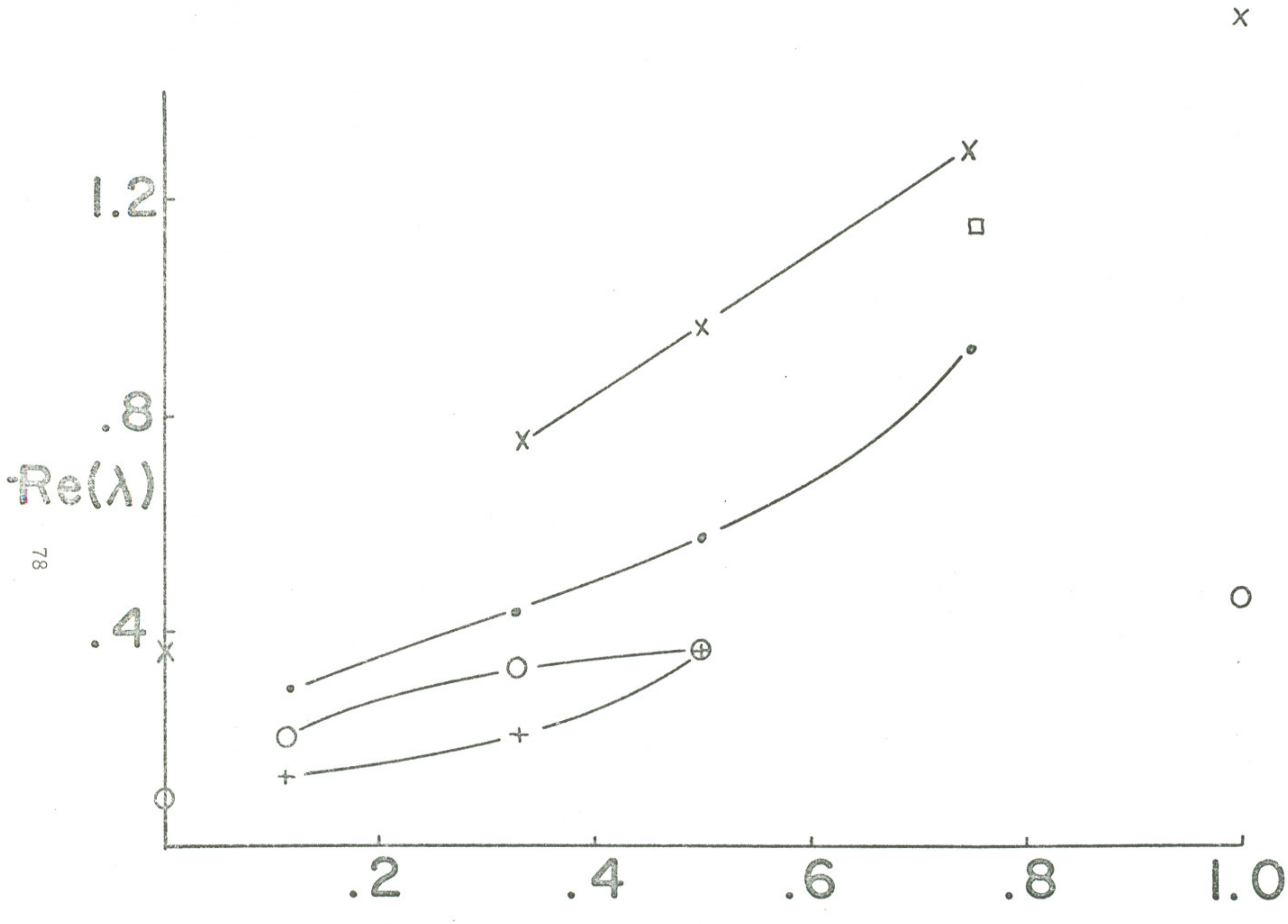


Figure 15-2

Recalling equation (2.2) and using equation (5.2) we have for the equation of state of a one-dimensional binary lattice gas with a hard sphere interaction potential

$$(\rho)^{-1} = \frac{-x_1 a e^{-Mu}}{1-e^{-u}} \qquad \frac{-e^{-u}}{1-e^{-u}} - M \quad /(ae^{-Mu}/(1-e^{-u}))$$

$$- \frac{-x_2 a e^{-MNu}}{1-e^{-u}} \quad \frac{e^{-u}}{1-e^{-u}} + M \quad /(ae^{-MNu}/(1-e^{-u})) \quad ,$$

$$(a\rho)^{-1} = e^{-u}/(1-e^{-u}) + M(1 + x_2 \, (N-1)) \quad ,$$

$$a\rho = (e^{u}-1)/((e^{u}-1)(1 + x_2(N-1)) + 1) \quad . \qquad (5.29)$$

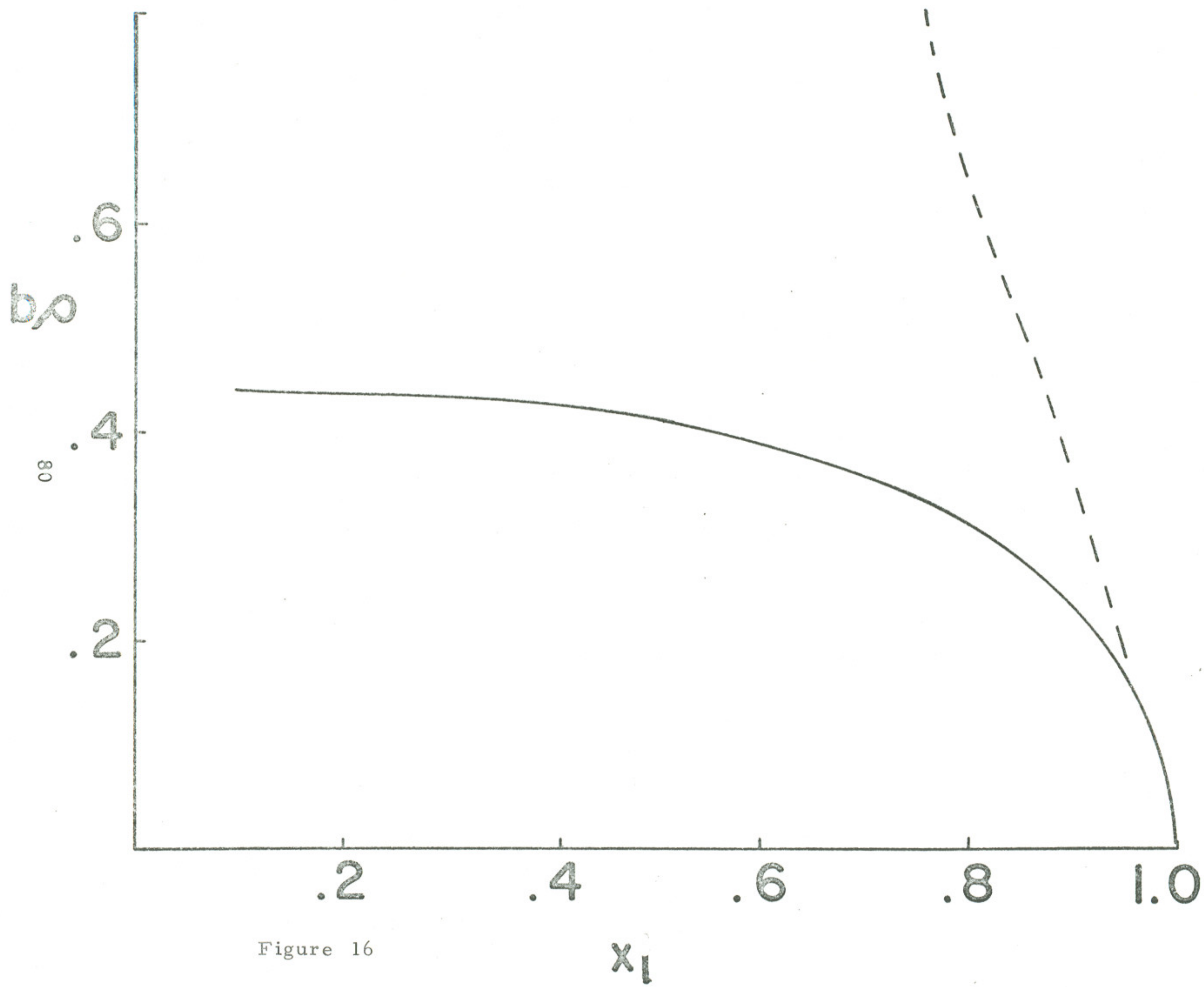


Figure 16

We have investigated the asymptotic behavior of the pair correlation function in a one-dimensional binary mixture interacting through a strictly nearest neighbor pair potential. Several cases were examined.

Case 1. -

Hard-sphere potential, linear continuum.

For this case the asymptotic form of G(r) is always a damped sinusoid. However, there is a locus generated in the (ρ, x_1) plane, across which, the asymptotic form of G(r) abruptly changes its spatial frequency.

Case 2. -

Hard-sphere potential, lattice gas.

In this case the asymptotic form of the pair correlation function is once again a damped sinusoid. If we let M be the ratio of the lattice constant to the hard-sphere diameter of the smaller species, and N be the ratio of the diameters, then when the product MN is an odd integer we generate two separate regions in the (ρ, x_1) plane. Each region is characterized by the value of the spatial frequency of the damped sinusoid associated with G(r). When MN is an even integer we have only a single frequency associated with the asymptotic decay of the pair correlation function.

Case 3. -

Square-well potential, linear continuum.

For this case the (ρ, T) plane is divided into several regions. Each region is once again characterized by the value of the spatial frequency associated with the damped sinusoidal decay of G(r). The zero frequency region corresponds to monotonic exponential decay.

The square-well results are all consistent with the idea that the attractive part of the pair potential governs the monotonic region and the repulsive part governs the oscillatory regions. This is the reason for the increase in the monotonic region with an increase in the concentration of the smaller species. As we increase x_1 we must go to higher and higher densities in order to maintain oscillatory decay. This is because the "effective distance" between two particles increases as we add the smaller species and subtract the larger. Our chosen particle thus "sees" fewer hard-core repulsions and thus finds itself in a more attractive environment, resulting in an increase in the region of monotonic decay.

A simple fluid interacting through a square-well pair potential with a well-width to hard-core diameter ratio R equal to one has an ω of approximately four associated with the damped sinusoidal decay of G(r). For a ratio of one-half the associated frequency is approximately 2.4. Figures (10.1) through (10.4) show that, as the concentration of the smaller species increases, the $\omega \sim 2$ region decreases while the $\omega \sim 4$ region increases. This can be understood in terms of the simple fluid results. Since we are concerned with the oscillatory regions the repulsive part of the pair potential will govern the behavior. At low x_1 the smaller particles "see" the large repulsions of the larger species and thus we are in a region of attractive to repulsive ratio less than one. Just as in the simple fluid case this generates a "low" ω (low relative to 4, the ω for a pure fluid). However, as we increase x_1 we begin to approach closer and closer to a simple pure fluid and the $\omega \sim 4$ region begins to dominate.

Studies by Throop and Fisk[2] have related the spatial frequency ω to the moments of the direct correlation function. For a one-dimensional system of hard spheres the direct correlation function is given exactly by[14]

$$C(r) = -1/(1-b\rho)^2 + \rho r/(1-b/)^2 \qquad r < b$$
$$= 0 \qquad r > b \;, \qquad (8.1)$$

where b is the hard-sphere diameter and ρ is the number density. Following Throop and Fisk the spatial frequency ω is given by

$$\omega = (C_2/(4C_4) + (1-C_0)^{1/2}/(2(-C_4)^{1/2}))^{1/2}, \tag{8.2}$$

where

$$C_{2j} = (\rho/(2j)) \int_0^{oo} r^{2j} C(r)\, dr \quad , \tag{8.3}$$

and explicitly

$$C_0 = P(P-2)/(2A) \quad , \tag{8.4}$$

$$C_2 = (b^2 P/2)(3P-4)/(12A) \quad , \tag{8.5}$$

$$C_4 = (b^4 P/24)(5P-6)/(30A) \quad , \tag{8.6}$$

$$A = (1-P)^2 \quad , \tag{8.7}$$

and

$$P = b\rho$$

Substituting equations (8.4) through (8.7) into equation (8.2) one obtains

$$\omega b = \frac{(3P-4)/(2A)}{(5P-6)/(15A)} + \frac{((2A-P(P-2)/(2A))^{1/2}}{(P(5P-6)/(180A))^{1/2}} \quad . \tag{8.9}$$

Figure (17) shows a plot of ωb versus $b\rho$ for ω given by equation (8.9) and ωb given by direct solution of the simple fluid equation. (Equation (3.11)). Also shown in the figure are the curves for $-\kappa b$ versus ρb from equation (3.11) and from the moment expansion method which gives $-\kappa$ as

$$-\kappa = -((1-C_o)^{1/2}/(2(-C_4)^{1/2}) - C_2/4C_4)^{1/2} \tag{8.10}$$

Equations (8.9) and (8.10) are based on truncation of the moment expansion of $\hat{C}(k)$. The Fourier transform of $C(r)$, at $0(k^4)$. For purely repulsive potentials such as hard spheres, this is the first acceptable approximation since truncation at $0(k^2)$ gives a divergent compressibility.

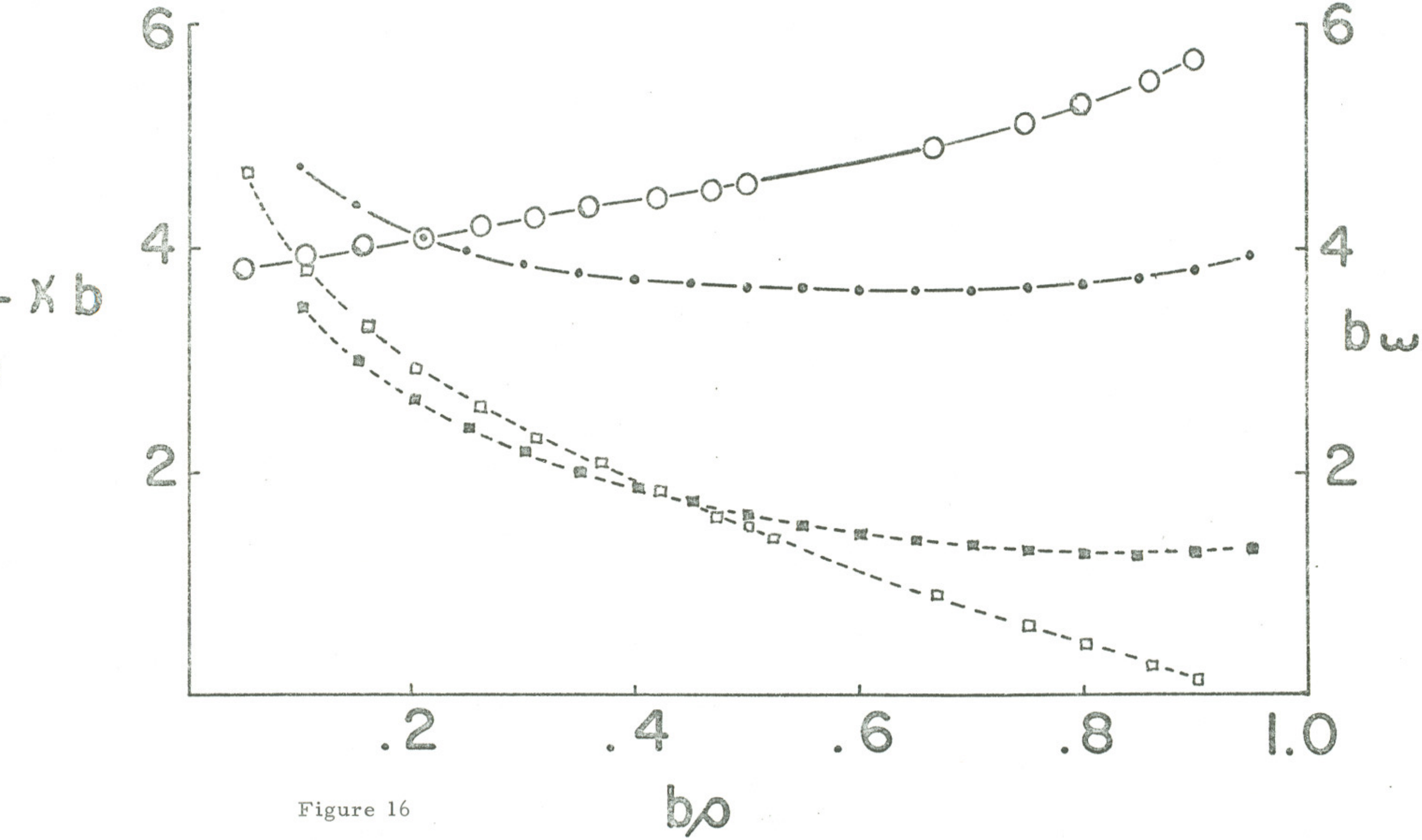


Figure 16

All of the moments of (8.1) are negative and if higher approximations for ωb only contain ratios of the moments like the k^4 case, then the effect will be to increase the value of ω for a given value of the density. From Figure (17) one can see that this is precisely what is needed to bring the moment expansion values in line with the direct solution values.

The position of the transition loci in the phase space of a real three dimensional fluid can be predicted by examining the position of the spinodal curve for a corresponding van der Waal's mixture. From equation (6.44) we have

$$T_2 = 2\rho\ (1-2\rho)^2 + \ \rho x_1\ (2-3\rho)\ ) \quad . \tag{8.11}$$

Equation (8.11) corresponds to our mixtures with $N = 2$, $H = 1$, and $R = 1$. Thus for all but very low densities the spinodal curve lies well within the region of monotonic decay. We may also examine the pseudocritical given by [9]

$$T_c = (8/27)a(x_1)/b(x_1) \tag{8.12}$$

and

$$P_c = (1/27)a(x_1)/b(x_1)^2 \quad , \tag{8.13}$$

where

$$a(a_1) = x_1^{\,2}\epsilon \ \ 2x_1(1-x_1)H^{1/2}\epsilon \ \ (1-x_1)^2 H\epsilon \quad ,$$

and

$$b(x_1) = x_1 b \quad (1-x_1)Nb \quad . \tag{8.14}$$

Thus setting $N = 2$ and $H = 1$, one obtains

$$k\,T_c/\epsilon \;=\; (0.296)/(2-x_1) \tag{8.15}$$

and

$$b\,P_c/\epsilon \;=\; (0.037)/(2-x_1)^2 \;. \tag{8.16}$$

These pseudocritical points lie below the spinodal (the true critical point lying on the spinodal) and thus are in the region of monotonic decay. One would then expect that for real systems the region of oscillatory decay will lie comparatively far away from the true (three dimensional) critical point.[1]

The transition loci may be experimentally investigated by means of x-ray or thermal neutron scattering studies. For a simple fluid of N systems each of scattering power f(k) the intensity I(k) of radiation of wavelength λ scattered through angle θ from the direction of a primary beam of intensity I_o at a distance R from the scatter is, in the first Born approximation, given by[15,16,17]

$$I(k) = I_o N f^2(k) r_o^2 \left((1+\cos^2\theta)/2R^2 \right) * \left(1+\rho\int_0^{\infty} \cos(kr)\; G(r)\; dr \right) , \tag{8.17}$$

where $k = 4\pi\lambda^{-1}\sin(\theta/2)$ and r_o is the "classical electron radius". With G(r) given by equation (1.9), equation (8.17) becomes[3]

$$I = \left((I(k)-1)/I_o(k) \right)/\rho = 2|Y_1|\left(A\kappa(\kappa^2+\omega^2+k^2) + B\omega\,(k^2-\kappa^2-\omega^2)\right)/\left((\kappa^2+\omega^2)^2+k^2(k^2+2(\kappa^2-\omega^2)) \right) \;, \tag{8.18}$$

where here we have set

$$I_o(k) = I_o N f^2(k) r_o^2 (1+\cos^2\theta)/(2R^2) \quad , \tag{8.19}$$

$$A = \cos(\arg(\gamma_1)) \quad , \tag{8.20}$$

and

$$B = \sin(\arg(\gamma_1)) \quad . \tag{8.21}$$

The $\omega = 0$ case is the well known form for monotonic decay of $G(r)$

$$I = (\gamma_1)/(\kappa^2 + k^2) \quad . \tag{8.22}$$

For a binary mixture of systems of scattering powers $f_1(k)$ and $f_2(k)$ the corresponding formula is[15]

$$I(k) = I_o N r_o^2 ((1+\cos^2\theta)/2R^2) \left[x_1 f_1^2(k) + (1-x_1) f_3^2(k) \right] + \rho \int_0^\infty \left[x_1^2 f_1^2(k) G_{11}(r) + (1-x_1)^2 f_2^2(k)\, G_{22}(r) + 2\, x_1 (1-x_1) f_1(k)\, f_2(k)\, G_{12}(r) \right] \cos kr\, dr \quad . \tag{8.23}$$

Unfortunately, because there are now two scattering powers, and three pair correlation functions, formulas corresponding to equations (8.18) and (8.22) cannot be obtained by substituting the asymptotic forms of the correlation functions into equation (8.23).

Further study of the effect on the transition loci of changes in the mixing parameters N, H, and R should help to clarify the meaning of the various oscillatory regions. The detail shown by the loci give us a valuable tool for investigating the parameters of the intermolecular pair potential and their contribution to the properties of the entire system.

APPENDIX A

Define -[8]

$$f_{11}(\gamma_1, \gamma_1') = f_{11}(-\gamma_1', -\gamma_1) \quad , \tag{1.1}$$

$$f_{22}(\gamma_2, \gamma_2') = f_{22}(-\gamma_2', -\gamma_2) \quad , \tag{1.2}$$

$$f_{12}(\gamma_1, \gamma_2') = f_{21}(-\gamma_2', -\gamma_1) \quad , \tag{1.3}$$

and

$$f_1(\gamma_1) = f_1(-\gamma_1) \quad , \tag{1.3}$$

$$f_2(\gamma_2) = f_2(-\gamma_2) \quad ,$$

then

$$f_1(\gamma_1) = \int_{-k+\gamma_1}^{L-k+\gamma_1} d\gamma_1' \, f_{11}(\gamma_1, \gamma_1') + \int_{-k+\gamma_1}^{L-k+\gamma_1} d_2' \, f_{12}(\gamma_1, \gamma_2') \quad ,$$

$$f_2(\gamma_2) = \int_{-k+\gamma_2}^{L-k+\gamma_2} d\gamma_2' f_{22}(\gamma_2, \gamma_2') + \int_{-k+\gamma_2}^{L-k+\gamma_2} d\gamma_1' f_{21}(\gamma_2, \gamma_1) \quad . \tag{1.4}$$

The normalizations are

$$x_1 = \int_{-L/2}^{L/2} d\gamma_1 f_1(\gamma_1) \quad ,$$

and

$$x_2 = \int_{-L/2}^{L/2} d\gamma_2 f_2(\gamma_2) \quad . \tag{1.5}$$

The entropy and the internal energy are then given by

$$\frac{S}{k_B M} = \int_{-L/2}^{L/2} d\gamma_1 f_1(\gamma_1) \ln f_1(\gamma_1) + \int_{-L/2}^{L/2} d\gamma_2 f_2(\gamma_2) \ln f_2(\gamma_2)$$

$$- \int_{-L/2}^{L/2} d\gamma_1 \int_{-k+\gamma_1}^{L-k+\gamma_1} d\gamma'_1 f_{11}(\gamma_1, \gamma'_1) \ln f_{11}(\gamma_1, \gamma'_1)$$

$$-2 \int_{-L/2}^{L/2} d\gamma_1 \int_{-k+\gamma_1}^{L-k+\gamma_1} d\gamma'_2 f_{12}(\gamma_1, \gamma'_2) \ln f_{12}(\gamma_1, \gamma'_2)$$

$$- \int_{-L/2}^{L/2} d\gamma_2 \int_{-k+\gamma_2}^{L-k+\gamma_2} d\gamma'_2 f_{22}(\gamma_2, \gamma'_2) \ln f_{22}(\gamma_2, \gamma'_2) \ , \qquad (1.6)$$

and

$$\frac{E}{M} = \int_{-L/2}^{L/2} d\gamma_1 \int_{-k+\gamma_1}^{L-k+\gamma_1} d\gamma'_1 \phi_{11}(\gamma, \gamma'_1) f_{11}(\gamma_1, \gamma'_1)$$

$$+2 \int_{-L/2}^{L/2} d\gamma_1 \int_{-k+\gamma_1}^{L-k+\gamma_1} d\gamma'_2 \phi_{12}(\gamma_1, \gamma'_2) f_{12}(\gamma_1, \gamma'_2)$$

$$+ \int_{-L/2}^{L/2} d\gamma_2 \int_{-k+\gamma_2}^{L-k+\gamma_2} d\gamma'_2 \phi_{22}(\gamma_2, \gamma'_2) f_{22}(\gamma_2, \gamma'_2) \ . \qquad (1.7)$$

The free energy $F = E - TS$ is then made a minimum with respect to f_1, f_2, f_{11}, f_{12}, and f_{22} under the additional conditions (1.1) and (1.3) to (1.5). Using undetermined multipliers λ_1 and λ_2 for equations (1.5), $2\lambda_3$ and $2\lambda_4$ for eqs. (1.4), $\lambda_5(\gamma_1)$ and $\lambda_6(\gamma_2)$ for eqs. (1.3), and $\lambda_7(\gamma_1, \gamma'_1)$ and $\lambda_8(\gamma_2, \gamma'_2)$ for eqs. (1.1), we have

$$-1 - \ln f_1(\gamma_1) + \lambda_1 + 2\lambda_3(\gamma_1) + \lambda_5(\gamma_1) - \lambda_5(-\gamma_1) = 0 \ , \qquad (1.8)$$

$$-1-\ln f_2(\gamma_2)+\lambda_2+2\lambda_4(\gamma_2)+\lambda_6(\gamma_2)-\lambda_6(-\gamma_2)=0 \quad , \tag{1.9}$$

$$\beta\phi_{11}(\gamma_1,\gamma_1')+1+\ln f_{11}(\gamma_1,\gamma_1')-2\lambda_3(\gamma_1)+\lambda_7(\gamma_1,\gamma_1')$$
$$-\lambda_7(-\gamma_1',-\gamma_1)=0 \tag{1.10}$$

$$\beta\phi_{22}(\gamma_2,\gamma_2')+1+\ln f_{22}(\gamma_2,\gamma_2')-2\lambda_4(\gamma_2)+\lambda_8(\gamma_2,\gamma_2')-\lambda_8(-\gamma_2',-\gamma_2)=0 \tag{1.11}$$

$$\beta\phi_{12}(\gamma_1,\gamma_2')+1+\ln f_{12}(\gamma_1,\gamma_2')-\lambda_3(\gamma_1)-\lambda_4(-\gamma_2')=0 \tag{1.12}$$

and

$$-F/MkT = x_1\lambda_1+(1-x_1)\lambda_2 \quad . \tag{1.13}$$

Combining equations (1.3) and (1.1) with eqs. (1.8) through (1.11), one can eliminate λ_5, λ_6, λ_7, and λ_8, so that the $f(\gamma)$'s and the $f(\gamma,\gamma')$'s are expressed using only λ_1, λ_2, λ_3, and λ_4.

After the elimination of λ_5 and λ_8 from equs. (1.1), (1.3), and (1.8) through (1.11), one obtains

$$\ln f_1(\gamma_1) = \lambda_3(\gamma_1)+\lambda_3(-\gamma_1)+\lambda_1-1 \quad ,$$
$$\ln f_2(\gamma_2) = \lambda_4(\gamma_2)+\lambda_4(-\gamma_2)+\lambda_2-1 \quad , \tag{1.14}$$

$$\ln f_{11}(\gamma_1,\gamma_1') = \lambda_3(\gamma_1)+\lambda_3(-\gamma_1')-\beta\phi_{11}(\gamma_1,\gamma_1')-1 \quad ,$$
$$\ln f_{22}(\gamma_2,\gamma_2') = \lambda_4(\gamma_2)+\lambda_4(-\gamma_2')-\beta\phi_{22}(\gamma_2,\gamma_2')-1 \quad , \tag{1.15}$$
$$\ln f_{12}(\gamma_1,\gamma_2') = \lambda_3(\gamma_1)+\lambda_4(-\gamma_2')-\beta\phi_{12}(\gamma_1,\gamma_2')-1 \quad .$$

Since $f(\gamma)$ L^{-1}, it is plausible to choose $\lambda_3(\gamma_1)$ and $\lambda_4(\gamma_2)$ of equation (1.14) so that $f_1(\gamma_1)$ and $f_2(\gamma_2)$ become constant. This reasoning gives one

$$\lambda_3(\gamma_1) = \xi_3 \gamma_1 + c_3 \quad ,$$
$$\lambda_4(\gamma_2) = \xi_4 \gamma_2 + c_4 \qquad (1.16)$$

λ_3 and λ_4 not necessarily being equal. Putting these into eqs. (1.15) and changing the primed coordinates into relative ones such that $r_{12} = \gamma'_2 + k - \gamma_1$ etc., one obtains

$$\ln f_{11}(\gamma_1, \gamma'_1) = \xi_3(k - r_{11}) + 2c_3 - 1 - \beta\phi_{11}(r_{11}) \quad ,$$
$$\ln f_{22}(\gamma_2, \gamma'_2) = \xi_4(k - r_{22}) + 2c_4 - 1 - \beta\phi_{22}(r_{22}) \quad , \qquad (1.17)$$
$$\ln f_{12}(\gamma_1, \gamma'_2) = \xi_4(k - r_{12}) + c_3 + c_3 + c_4 - 1 - \beta\,\phi_{12}(r_{12})$$
$$+ (\xi_3 - \xi_4)\gamma_1 \quad .$$

Of these three relations, f_{11} and f_{22} are functions only of the relative coordinates. Therefore it is reasonable to conclude that f_{12} also depends only on the relative coordinate r_{12}, to obtain

$$\xi_3 = \xi_4 = \xi \quad . \qquad (1.18$$

Combining equations (1.16) and (1.18), one obtains

$$\lambda_3(\gamma_1) = \xi\gamma_1 + c_3 \quad ,$$
$$\lambda_4(\gamma_2) = \xi\gamma_2 + c_4 \quad , \qquad (1.19)$$

ξ, c_3, and c_4 being constants. Determining c_3 and c_4 from equation (1.5), one obtains

$$f_{11}(\gamma_1, \gamma'_1) = x_1 L^{-1} \exp(-\lambda_1 + \xi(k - r_{11})\beta\phi_{11}(r_{11})) \quad ,$$

$$f_{22}(\gamma_2,\gamma_2') = x_2 L^{-1} \exp(-\lambda_2 + \xi(k-r_{22}) - \beta\phi_{22}(r_{22})) \quad ,$$

$$f_{12}(\gamma_1,\gamma_2') = (x_1 x_2)^{1/2} L^{-1} \exp(-\tfrac{1}{2}(\lambda_1+\lambda_2) + \xi(k-r_{12}) - \beta\phi_{12}(r_{12}) . \quad (1.20)$$

and also

$$f_1(\gamma_1) = x_1 L^{-1} \quad ,$$

$$f_2(\gamma_2) = x_2 L^{-1} \quad . \quad (1.21)$$

Inserting equations (1.20) and (1.21) into equations (1.4), one obtains

$$e^{-\xi k} = \exp(-\lambda_1 - \beta\mu_1) + \exp(-t\,\frac{1}{2}(\lambda_1+\lambda_2) - \beta\mu_{12}) \quad , \quad (1.22)$$

$$e^{-\xi k} = \exp(t - \frac{1}{2}(\lambda_1+\lambda_2) - \beta\mu_{12}) + \exp(-\lambda_2 - \beta\mu_{22}) \quad , \quad (1.23)$$

where

$$e^{t} = (x_1/x_2)^{1/2}$$

and, where we have defined

$$e^{-\beta\mu_{11}(\xi)} \equiv \int_0^{\infty} dr\, e^{-\xi r - \beta\phi_{11}(r)} \quad (1.25)$$

$\mu_{22}(\xi)$ and $\mu_{12}(\xi)$ are defined when one replaces $\phi_{11}(r)$ in equation (1.25) by $\phi_{22}(r)$ and $\phi_{12}(r)$, respectively. Solutions of equations (1.22) and (1.23) are

$$e^{-\lambda_1} = \exp(\beta\mu_{11} - \xi k)(\Gamma - 1 + 2x_1)/(\Gamma+1) \quad ,$$

$$e^{-\lambda_2} = \exp(\beta\mu_{22} - \xi k)(\Gamma + 1 - 2x_1)/(\Gamma+1) \quad , \quad (1.26$$

where

$$\Gamma^2 \equiv 1 + 4x_1 x_2 (e^{+\beta\omega(\xi)} - 1) \quad , \quad (1.27)$$

and $$\omega(\xi) = 2\mu_{12} - \mu_{22} - \mu_{11} \quad . \tag{1.28}$$

Inserting equation (1.26) into equation (1.13), one obtains

$$-F/MkT = \xi k + \ln(\Gamma+1) - x_1(\beta\ \mu_{11} + \ln(\Gamma-1+2x_1)) \\ -x_2(\beta\mu_{22} + \ln(\Gamma+1-2x_1)). \tag{1.29}$$

ξ is determined from the condition that F of equation (1.29) is made a minimum with respect to ξ, keeping k and T constant. Combining equations (1.20) and (1.26), the final results for the f_{ij}'s are

$$f_{11}(\gamma_1, \gamma_1') = x_1 L^{-1} \frac{(\Gamma-1+2x_1)}{(\Gamma+1)} \exp(-\beta\mu_{11} - \xi r_{11}(\beta\phi_{11}(r_{11})) \quad ,$$

$$f_{22}(\gamma_2, \gamma_2') = x_2 L^{-1} \frac{(\Gamma+1-2x_1)}{(\Gamma+1)} \exp(-\beta\mu_{22} - \xi r_{22} - \beta\phi_{22}(r_{22})) \quad ,$$

$$f_{12}(\gamma_1, \gamma_2') = \frac{2x_2 L^{-1}}{(\Gamma+1)} \exp(-\beta\mu_{12} - \xi r_{12} - \beta\phi_{12}(r_{12})) \quad ,$$

and

$$f_{21}(\gamma_2, \gamma_1') = \frac{2x_1 L^{-1}}{(\Gamma+1)} \exp(-\beta\mu_{21} - \xi r_{21} - \rho\phi_{21}(r_{21})) \quad .$$

APPENDIX B

Muller's Method-[11]

Start: zo,z1,z2, are the initial estimates.

$$f_o = P(zo),\ f_1 = P(z1),\ f_2 = P(z2)$$

$$\lambda_2 = (z2-z1)/(z1-zo)$$

Iterative algorithm:

$$\delta_i = 1 + \lambda_i$$

$$g_i = f_i - 2\lambda_i^2 - f_{i-1}\delta_i^2 + f_i(\lambda_i + \delta_i) \quad ,$$

$$\lambda_i + 1 = -2f_i\delta_i / G_i \quad ,$$

$$G_i = g_i \pm (g_i^2 - 4f_i\delta_i\lambda_i(f_{i-2}\lambda_i - f_{i-1}\delta_i + f_i))^{1/2} \quad ,$$

$$h_i = (\lambda_i + 1)h_i \quad ,$$

$$x_i + 1 = z_i + h_{i+1} \quad .$$

Comments: The method is based on quadratic interpolation of the last three estimates. Its rate of convergence is 1.839. It is more efficient than other methods for $n \geq 85$. Note: For the transcendental functions under consideration $n \rightarrow \infty$.

APPENDIX B

FORTRAN V PROGRAM FOR MULLER'S METHOD

FLOW CHART

Define Complex Variables

Define Real Variables

Dimension Variables

↓

DØ 45 L = 1,10
u(L) = 0.0 + 0.10*L
45 CØntinue

↓

DØ 46 K = 1,5
V(k) = 0.0 + 0.1*K
46 CØntinue

↓

DØ 47 K = 6, 10
V(k) = 0.0 1.0*(K-5)
47 CØntinue

↓

Write (6,3)
3 FØrmat (IH '   ')

↓

DØ 747 JJ = 1,9

↓

THETA = 0.10*JJ
Write (6,21) THETA

↓

B 1 (0) = 0
B 2 (0) = 0
Z 1 (0) = 0
Z 3 (0) = 0
Z 4 (0) = 0

↓

u(0) = 0
V(0) = 0

↓

DØ 100 L = 1, 10

↓

J = 1
J = 1

↓

DØ 101 K = 1,10

↓

103 FORMAT (1H02F 12.8)
21 FORMAT (2E20.8)
27 FORMAT (1H08E 16.8)

↓

R = 1.0
N = 2.0
MM = 1.0

↓

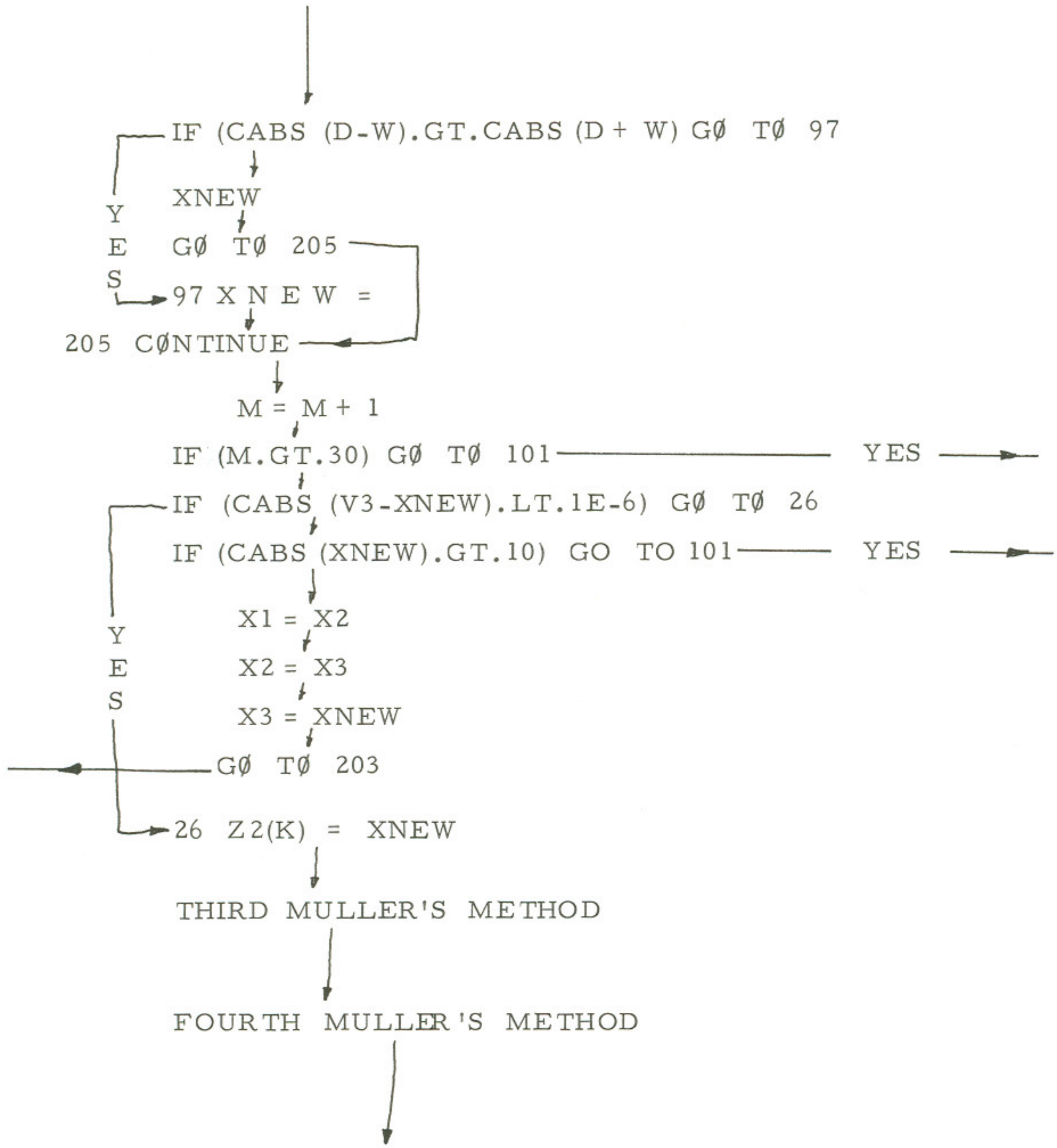
A1 =
A2 =
A3 =
V4 =
A4 =
GAMMA =
C1 =
C2 =

↓

FIRST MUELLER'S METHOD

```
      X1 = CMPLX (      )
      X2 = CMPLX (      )
      X3 = CMPLX (      )
           M = 1
 202  CALL FCN (      )
      FF3 =
      CALL FCN (      )
      FF2 =
      CALL FCN (      )
      FF3 =
      LAM =
      DEL =
      D   =
      W   =
      IF (CABS (D-W).GT.CABS(D+W) GØTØ 96
      X NEW =
      IF (REAL (XNEW).GT.0.0) GØTØ 49
      GO TO 151
   49 XNEW = -XNEW
  151 IF(ABS(AIMAG(XNEW)).GT.1,DE-6) GØTØ 614
      GO TO 204
  614 XNEW = REAL(XNEW)
      GO TO 204
   96 XNEW =
      IF (REAL(XNEW).GT.0.0) GØTØ 48
      GO TO 152
   48 XNEW = -XNEW
  152 IF(ABS(AIMAG(XNEW)).GT . 1.0E-b) GØTØ 615
      GO TO 204
  615 XNEW = REAL(XNEW)
```

```
204 CØNTINUE
    M = M + 1
    IF (M GT. 30) 60 TO 101          YES
    IF (CABS (X3-XNEW).LT.1.0E-6) GO TØ 24
    IF (CABS (XNEW).GT.10) GØ TØ 101          YES
    X1 = X2
    X2 = X3
    X3 = XNEW
    GØ TØ 2Ø2
24  X1 (K) = XNEW
SECOND MULLER'S METHOD
    X1 = Z1(K) + 0.1
    X2 = Z1(K) + 0.12
    X3 = Z1(K) + 0.16
        M = 1
203 CALL FCN( )
    FF3 =
    CALL FCN(   )
    FF2 =
    CALL FCN(   )
    FF1 =
    LAM =
    DEL =
    D =
    W =
```


IF (CABS (D-W).GT.CABS (D + W) GØ TØ 97
XNEW
GØ TØ 205
YES
97 X N E W =
205 CØNTINUE
M = M + 1
IF (M.GT.30) GØ TØ 101
YES
IF (CABS (V3-XNEW).LT.1E-6) GØ TØ 26
IF (CABS (XNEW).GT.10) GO TO 101
YES
X1 = X2
X2 = X3
X3 = XNEW
YES
GØ TØ 203
26 Z2(K) = XNEW
THIRD MULLER'S METHOD
FOURTH MULLER'S METHOD

```
B1(K) = AMIN1 (ABS(REAL(X1 - 4(K))))

IF (ABS(B1(K) - ABS(REAL(Z1(K)))).LT.1E-4) GØ TØ 1      YES -> 1
IF (ABS)    . . .   Z2    ) GØ TØ 2                      YES -> 2
IF (ABS)    . . .   Z3    ) GØ TØ 4                      YES -> 4
IF (ABS)    . . .   Z4    ) GØ TØ 5                      YES -> 5

B11(K) = CMPLX (B1(K), AIMAG (Z1(K)))
1   GØ TØ 31
2   B11 (K) =   . . .   Z2
    GØ TØ 31
4   B11(K) =    . . .   Z3
    GØ TØ 31
5   B11 (K) =

31 IF(ABS (AIMAG (B11(K))).GT 1.)  GØ TØ 30   YES ->

IF (I.EQ.2)  GØ  TØ  33   YES ->

WRITE (6,103) U(L), V(K-1)
WRITE (6,27)Z1(K-1), Z2(K-1), Z3(k-1), Z4(K-1)
WRITE (6,103) U(L),  V(K)
WRITE (6,27) Z1(K), Z2(K), Z3(K), Z4(K)
```

```
I = 2

33 B1(K) = AMINI (ABS REAL (Z2 - 4(K))))

YES  IF (ABS(B1(K) - ABS(REAL (Z2(K)))).LT.1E-4) GØ TØ 6
YES  IF (        . . .        Z3        ) GØ TØ 7
YES  IF (        . . .        Z4        ) GØ TØ 8

6 B11(K) = CMPLX(B1(K), AIMAG(Z2(K)))
         GØ TØ 30
7 B11(K) =       . . .        Z3
         GØ TØ 30
8 B11(K) =       . . .        Z4

30 IF (ABS(ABS(AIMAG(B11(K))) - 2.).GT.1.) GØ TØ 40
   YES
         GØ TØ 102

40 IF (J.EQ.2) GØ TØ 102

         WRITE (6,103) U(L), V(K-1)
         WRITE (6,27) Z1(K-1), Z2(K-1), Z3(K-1), Z4(K-1)
         WRITE (6,103) U(L), V(K)
         WRITE (6,27) Z1(K), Z2(K), Z3(K), Z4(K)
```

```
CALL  FCN (Z1(K), R, N, U(L), V(K), C1, C2, FNEW1)

CALL  FCN (Z2(K)                              FNEW2)

CALL  FCN(Z3(K)                               FNEW3)

CALL  FCN(Z4(K)                               FNEW4)

WRITE (6,27)  FNEW1,  FNEW2,  FNEW3,  FNEW4

         J = 2

102  IF (I + J.EQ.4)  GØ  TØ  100 ----
                                     Y
      101      CONTINUE              E
                                     S
      100      CONTINUE  -------------

      747      CONTINUE

         STOP

      SUBROUTINE  FCN(A, B, C, D, G, H, P, F)

      RETURN
      END
```

```
PERRY-PNC/LIB$  CREATE:03/29/73,15:53:07 FREQ:5 SIZE:11 KIND:DISK KEY:1 LIFE:
PERM ACCESS:UPDATE
IL
      C      THIS PROGRAM FINDS THE  ROOTS OF A COMPLEX-VALUED FUNCTION F(
      C      USING MUELLER'S METHOD
             COMPLEX XNEW,X1,X2,X3,FF1,FF2,FF3,LAM,DEL,D,W,Z1,Z2,Z3,Z4
            1 ,G1,G2,G3,F1,F2,F3,FFF1,FFF2,FFF3,B11
            1    ,FNEW1,FNEW2,FNEW3,FNEW4
             REAL N,MM
             DIMENSION U(15),V(15),Z1(15),Z2(15),Z3(15),Z4(15),
            1   B1(15),B2(15),B11(15)
              DO 45 L=1,10
              U(L)=0.00+0.10*L
          45 CONTINUE
             DO 46 K=1,5
             V(K)=0.00+0.10*K
          46 CONTINUE
             DO 47 K=6,10
             V(K)=0.00+1.00*(K-5)
          47 CONTINUE
      C      THIS BEGINS THE LOOPING PROCEDURE FOR      SOLUTION OF THE EQU
             WRITE(6,3)
           3 FORMAT(1H 'SQ.-WELL,R=1,N=2,MM=1   ')
             DO 747 JJ=8,9
             THETA=0.10*JJ
             WRITE(6,21) THETA
             B1(0)=0
             B2(0)=0
             Z1(0)=0
             Z3(0)=0
             Z4(0)=0
             U(0)=0
             V(0)=0
             DO 100 L=1,10
             J=1
             I=1
             DO 101 K=1,10
         103 FORMAT(1H02F12.8)
          21 FORMAT(2E20.8)
          27 FORMAT(1H08E16.8)
             R=1.0
              N=2.0
              MM=1.0
              A1=1.-EXP(-R*U(L))+EXP(-R*U(L)-V(K))
              A2=1.-EXP(-R*N*U(L))+EXP(-R*N*U(L)-MM*V(K))
              A3=1.-EXP(-(R*(N+1.)/2.)*U(L))+EXP(-(R*(N+1.)/2.)*U(L)
            1   -MM**.5*V(K))
              V4=(MM+1.-2.*MM**.5)*V(K)
              A4=EXP(V4)*A1*A2/(A3*A3)
             GAMMA=SQRT(1.0+4.0*THETA*(1.0-THETA)*(A4-1.0))
             C1=GAMMA
             C2=THETA
             X1=CMPLX(-0.1,-0.1)
             X2=CMPLX(-0.15,-0.15)
```

```
      X3=CMPLX(-0.2,-0.2)
      M=1
  202 CALL FCN(X3,R,N,U(L),V(K),C1,C2,FFF3)
      FF3=FFF3/X3
      CALL FCN(X2,R,N,U(L),V(K),C1,C2,FFF2)
      FF2=FFF2/X2
      CALL FCN(X1,R,N,U(L),V(K),C1,C2,FFF1)
      FF1=FFF1/X1
      LAM=(X3-X2)/(X2-X1)
      DEL=1.+LAM
      D=FF1*LAM**2-FF2*DEL**2+FF3*(LAM+DEL)
      W=CSQRT(D**2-4.*FF3*DEL*LAM*(FF1*LAM-FF2*DEL+FF3))
      IF(CABS(D-W).GT.CABS(D+W)) GO TO 96
      XNEW=X3+(X3-X2)*(-2.*FF3*DEL)/(D+W)
      IF(REAL(XNEW).GT.0.0) GO TO 49
      GO TO 151
   49 XNEW=-XNEW
  151 IF(ABS(AIMAG(XNEW)).GT.1.0E-6) GO TO 614
      GO TO 204
  614 XNEW=REAL(XNEW)
      GO TO 204
   96 XNEW=X3+(X3-X2)*(-2.*FF3*DEL)/(D-W)
      IF(REAL(XNEW).GT.0.0) GO TO 48
      GO TO 152
   48 XNEW=-XNEW
  152 IF(ABS(AIMAG(XNEW)).GT.1.0E-6) GO TO 615
      GO TO 204
  615 XNEW=REAL(XNEW)
  204 CONTINUE
      M=M+1
      IF(M.GT.30) GO TO 101
      IF(CABS(X3-XNEW).LT.1.0E-6) GO TO 24
      IF(CABS(XNEW).GT.10.) GO TO 101
      X1=X2
      X2=X3
      X3=XNEW
      GO TO 202
   24 Z1(K)=XNEW
      X1=Z1(K)+0.1
      X2=Z1(K)+0.12
      X3=Z1(K)+0.16
      M=1
  203 CALL FCN(X3,R,N,U(L),V(K),C1,C2,FFF3)
      FF3=FFF3/(X3*(X3-Z1(K))*(X3-CONJG(Z1(K))))
      CALL FCN(X2,R,N,U(L),V(K),C1,C2,FFF2)
      FF2=FFF2/(X2*(X2-Z1(K))*(X2-CONJG(Z1(K))))
      CALL FCN(X1,R,N,U(L),V(K),C1,C2,FFF1)
      FF1=FFF1/(X1*(X1-Z1(K))*(X1-CONJG(Z1(K))))
      LAM=(X3-X2)/(X2-X1)
      DEL=1.+LAM
      D=FF1*LAM**2-FF2*DEL**2+FF3*(LAM+DEL)
      W=CSQRT(D**2-4.*FF3*DEL*LAM*(FF1*LAM-FF2*DEL+FF3))
      IF(CABS(D-W).GT.CABS(D+W))GO TO 97
      XNEW=X3+(X3-X2)*(-2.*FF3*DEL)/(D+W)
```

```
      GO TO 205
   97 XNEW=X3+(X3-X2)*(-2.*FF3*DEL)/(D-W)
  205 CONTINUE
      M=M+1
      IF(M.GT.30)GO TO 101
      IF(CABS(X3-XNEW).LT.1.E-6) GO TO 26
      IF(CABS(XNEW).GT.10.) GO TO 101
      X1=X2
      X2=X3
      X3=XNEW
      GO TO 203
   26 Z2(K)=XNEW
      X1=Z2(K)+0.1
      X2=Z2(K)+0.12
      X3=Z2(K)+0.16
      M=1
  207 CALL FCN(X3,R,N,U(L),V(K),C1,C2,FFF3)
      FF3=FFF3/(X3*(X3-Z1(K))*(X3-CONJG(Z1(K)))
     1*(X3-Z2(K))*(X3-CONJG(Z2(K))))
      CALL FCN(X2,R,N,U(L),V(K),C1,C2,FFF2)
      FF2=FFF2/(X2*(X2-Z1(K))*(X2-CONJG(Z1(K)))*
     1(X2-Z2(K))*(X2-CONJG(Z2(K))))
      CALL FCN(X1,R,N,U(L),V(K),C1,C2,FFF1)
      FF1=FFF1/(X1*(X1-Z1(K))*(X1-CONJG(Z1(K)))*
     1(X1-Z2(K))*(X1-CONJG(Z2(K))))
      LAM=(X3-X2)/(X2-X1)
      DEL=1.+LAM
      D=FF1*LAM**2-FF2*DEL**2+FF3*(LAM+DEL)
      W=CSQRT(D**2-4.*FF3*DEL*LAM*(FF1*LAM-FF2*DEL+FF3))
      IF(CABS(D-W).GT.CABS(D+W))GO TO 98
      XNEW=X3+(X3-X2)*(-2.*FF3*DEL)/(D+W)
      GO TO 210
   98 XNEW=X3+(X3-X2)*(-2.*FF3*DEL)/(D-W)
  210 CONTINUE
      M=M+1
      IF(M.GT.30)GO TO 101
      IF(CABS(X3-XNEW).LT.1.E-6) GO TO 29
      IF(CABS(XNEW).GT.10.) GO TO 101
      X1=X2
      X2=X3
      X3=XNEW
      GO TO 207
   29 Z3(K)=XNEW
      X1=Z3(K)+0.1
      X2=Z3(K)+0.12
      X3=Z3(K)+0.16
      M=1
  407 CALL FCN(X3,R,N,U(L),V(K),C1,C2,F3)
      G3=(X3*(X3-Z1(K))*(X3-CONJG(Z1(K)))*
     1(X3-Z2(K))*(X3-CONJG(Z2(K)))*(X3-Z3(K))*(X3-CONJG(Z3(K))))
      FF3=F3/G3
      CALL FCN(X2,R,N,U(L),V(K),C1,C2,F2)
      G2=(X2*(X2-Z1(K))*(X2-CONJG(Z1(K)))*
     1(X2-Z2(K))*(X2-CONJG(Z2(K)))*(X2-Z3(K))*(X2-CONJG(Z3(K))))
```

```
      FF2=F2/G2
      CALL FCN(X1,R,N,U(L),V(K),C1,C2,F1)
      G1=(X1*(X1-Z1(K))*(X1-CONJG(Z1(K)))*
     1(X1-Z2(K))*(X1-CONJG(Z2(K)))*(X1-Z3(K))*(X1-CONJG(Z3(K))))
      FF1=F1/G1
      LAM=(X3-X2)/(X2-X1)
      DEL=1.+LAM
      D=FF1*LAM**2-FF2*DEL**2+FF3*(LAM+DEL)
      W=CSQRT(D**2-4.*FF3*DEL*LAM*(FF1*LAM-FF2*DEL+FF3))
      IF(CABS(D-W).GT.CABS(D+W))GO TO 99
      XNEW=X3+(X3-X2)*(-2.*FF3*DEL)/(D+W)
      GO TO 500
   99 XNEW=X3+(X3-X2)*(-2.*FF3*DEL)/(D-W)
  500 CONTINUE
      M=M+1
      IF(M.GT.30)GO TO 101
      IF(CABS(X3-XNEW).LT.1.E-6) GO TO 32
      IF(CABS(XNEW).GT.10.) GO TO 101
      X1=X2
      X2=X3
      X3=XNEW
      GO TO 407
   32 Z4(K)=XNEW
      B1(K)=AMIN1(ABS(REAL(Z1(K))),ABS(REAL(Z2(K))),ABS(REAL(Z3(K))
     1    ,ABS(REAL(Z4(K))))
      IF(ABS(B1(K)-ABS(REAL(Z1(K)))).LT.1.E-4) GO TO 1
      IF(ABS(B1(K)-ABS(REAL(Z2(K)))).LT.1.E-4) GO TO 2
      IF(ABS(B1(K)-ABS(REAL(Z3(K)))).LT.1.E-4) GO TO 4
      IF(ABS(B1(K)-ABS(REAL(Z4(K)))).LT.1.E-4) GO TO 5
    1 B11(K)=CMPLX(B1(K),AIMAG(Z1(K)))
      GO TO 31
    2 B11(K)=CMPLX(B1(K),AIMAG(Z2(K)))
      GO TO 31
    4 B11(K)=CMPLX(B1(K),AIMAG(Z3(K)))
      GO TO 31
    5 B11(K)=CMPLX(B1(K),AIMAG(Z4(K)))
   31 IF(ABS(AIMAG(B11(K))).GT.1.) GO TO 30
      IF(I.EQ.2) GO TO 33
      WRITE(6,103)U(L),V(K-1)
      WRITE(6,27)Z1(K-1),Z2(K-1),Z3(K-1),Z4(K-1)
      WRITE(6,103)U(L),V(K)
      WRITE(6,27)Z1(K),Z2(K),Z3(K),Z4(K)
      I=2
   33 B1(K)=AMIN1(ABS(REAL(Z2(K))),ABS(REAL(Z3(K))),ABS(REAL(Z4(K))
      IF(ABS(B1(K)-ABS(REAL(Z2(K)))).LT.1.E-4) GO TO 6
      IF(ABS(B1(K)-ABS(REAL(Z3(K)))).LT.1.E-4) GO TO 7
      IF(ABS(B1(K)-ABS(REAL(Z4(K)))).LT.1.E-4) GO TO 8
    6 B11(K)=CMPLX(B1(K),AIMAG(Z2(K)))
      GO TO 30
    7 B11(K)=CMPLX(B1(K),AIMAG(Z3(K)))
      GO TO 30
    8 B11(K)=CMPLX(B1(K),AIMAG(Z4(K)))
   30 IF(ABS(ABS(AIMAG(B11(K)))-2.).GT.1.) GO TO 40
      GO TO 102
```

```
   40 IF(J.EQ.2) GO TO 102
      WRITE(6,103)U(L),V(K-1)
      WRITE(6,27)Z1(K-1),Z2(K-1),Z3(K-1),Z4(K-1)
      WRITE(6,103)U(L),V(K)
      WRITE(6,27)Z1(K),Z2(K),Z3(K),Z4(K)
      CALL FCN(Z1(K),R,N,U(L),V(K),C1,C2,FNEW1)
      CALL FCN(Z2(K),R,N,U(L),V(K),C1,C2,FNEW2)
      CALL FCN(Z3(K),R,N,U(L),V(K),C1,C2,FNEW3)
      CALL FCN(Z4(K),R,N,U(L),V(K),C1,C2,FNEW4)
      WRITE(6,27)FNEW1,FNEW2,FNEW3,FNEW4
      J=2
  102 IF(I+J.EQ.4) GO TO 100
  101 CONTINUE
  100 CONTINUE
  747 CONTINUE
      STOP
      SUBROUTINE FCN(A,B,C,D,G,H,P,F)
       COMPLEX F,A,D11,D12,D22,T3,T1,T2
       REAL  C11,C22,C,D,G,H,P
       C11=(H-1.+2.*P)/(H+1.)
       C22=(H+1.-2.*P)/(H+1.)
       D11=1.-CEXP(-B*(A+D))+CEXP(-B*(D+A)-G)
       D12=1.-CEXP(-((C+1.)/2.)*B*(A+D))
     1  +CEXP(-((C+1.)/2.)*B*(A+D)-MM**.5*G)
       D22=1.-CEXP(-C*B*(A+D))+CEXP(-C*B*(A+D)-MM*G)
       T3=D*4.*P*(1.-P)*CEXP(-(C+1.)*A)*(D12*D12
     1    -EXP(V4)*D11*D22)
       T3=T3/((D+A)*(H*H+1.)*A3*A3)
       T1=(C11*CEXP(-A)*D11)/A1
       T2=(C22*CEXP(-C*A)*D22)/A2
       F=D*(T1+T2+T3)-D-A
      RETURN
      END
```

APPENDIX C

Comparison of equation (2.2) with other work.

Recall equation (2.2)

$$-\rho^{-1} = x_1 J_{11}'(\xi)/J_{11}(\xi) + x_2 J_{22}'(\xi)/J_{22}(\xi) + \frac{\partial C}{\partial \xi} \quad , \tag{2.2}$$

where $$C = -\ln(\Gamma+1) + x_1 \ln(\Gamma - + 2x_1) = x_2 \ln(\Gamma + 1 - 2x_1) \tag{2.3}$$

Let $\phi_{ij}(r)$ be a hard-sphere interaction and equation (2.2) reduces to

$$b\rho = u/(u(1+ x_2(N-1)) + 1) \quad , \tag{C1}$$

where $$u = b\xi \quad .$$

If we let $N = 1$, or $x_1 = 1$, equation (C-1) reduces to the correct simple fluid form.

C.C. Carter[9] gives the equation of state for a van der Waal's mixture of hard-spheres as

$$\pi = 1/(\ell - \delta(x)) \quad , \tag{C-2}$$

where $$\pi = p/kT = \xi \quad , \tag{C-3}$$

$$\ell = 1/\rho \quad , \tag{C-4}$$

and $$\delta(x) = (1-x_2)b + x_2 Nb \quad . \tag{C-5}$$

Substituting (C-3) through (C-5) into equation (C-2), one obtains

$$\xi = 1/(1/\rho - (1-x_2)b - x_2 Nb)$$

$$b\rho = -1(-1 + x_2(1-N) - 1/\xi b)$$

or, with $u = b\xi$,

$$b\rho = u/(u(1+ x_2(N-1)) + 1) \quad . \tag{C-6}$$

Lebowitz and Zomick[6] use the following relation for the equation of state of a one-dimensional hard-sphere system:

$$P = (\rho_1 + \rho_2)/(1-\xi) \quad , \tag{C-7}$$

with

$$P = p/kT \quad , \tag{C-8}$$

$$\rho_i = x_i\rho \quad , \tag{C-9}$$

and

$$\xi = \rho_1 b - Nb\rho_2 \quad . \tag{C10}$$

Using equations (C-8) through (C-10) along with (C-7) one obtains

$$P = \rho/(1-b/(1-x_2 + Nx_2)$$

$$bP = b\rho/(1-b/(x_2(N-1) + 1)) \; ,$$

or with $u = bp/kT$ we have

$$b\rho = u/(u(x_2(N-1) + 1) + L) \quad . \tag{C-11}$$

If we let $\phi_{ij}(r)$ be a square-well interaction and take the simple fluid limit, equation (2.2) reduces to

$$(b\rho)^{-1} = 1 + 1/u - e^{-u}(1-e^{-v})/(1-e^{-u}(1-e^{-v})) \quad . \tag{C-12}$$

Katsura and Tago[10] give the equation of state of a one-dimensional square-well system as

$$\rho^{-1} = 1 + t^{-1} - (f/((1+f)e^{t} - f)) \quad , \tag{C-13}$$

where

$$f = e^{\beta\epsilon} - 1 = e^{v} - 1 \quad , \tag{C-14}$$

and $$t = p/kT = u \quad (\text{here } b = 1) \quad . \tag{C-15}$$

Substituting (C-14) and (C-15) into equation (C-13), one obtains

$$(b\rho)^{-1} = 1 + 1/u - (e^{v}-1)/(e^{v}e^{u}+1) \quad ,$$

or $$(b\rho)^{-1} = 1 + 1/u - e^{-u}(1-e^{-v})/(1-e^{-u}(1-e^{-v})) \quad . \tag{C-16}$$

APPENDIX D

Consider the equation for a simple fluid of hard spheres with hard-sphere diameter equal to b

$$bP/kT(e^{-b\sigma}) = bP/kT + b\sigma \quad , \tag{D-1}$$

Now let $u = bP/kT$, and $\lambda = b\sigma$. We then obtain ,

$$ue^{-\lambda} = u + \lambda \quad . \tag{D-2}$$

This equation is solved for complex λ and Figure D-1 shows a plot of $-Re(\lambda)$ versus u. (Labeled 'Pure A') As usual the λ plotted is the one of largest real part.

If we now look at a second hard sphere fluid with a hard-sphere diameter equal to 2b, the equation is

$$2bP/kT(e^{-2b\sigma}) = 2bP/kT + 2b\sigma \quad . \tag{D-3}$$

If we now define

$$u = 2bP/kT$$

and

$$\lambda = 2b\sigma$$

We again arrive at equation (D-2). However, if we wish to keep the definitions of u and λ the same so that we can plot the solutions on the same graphs equation (D-e) becomes

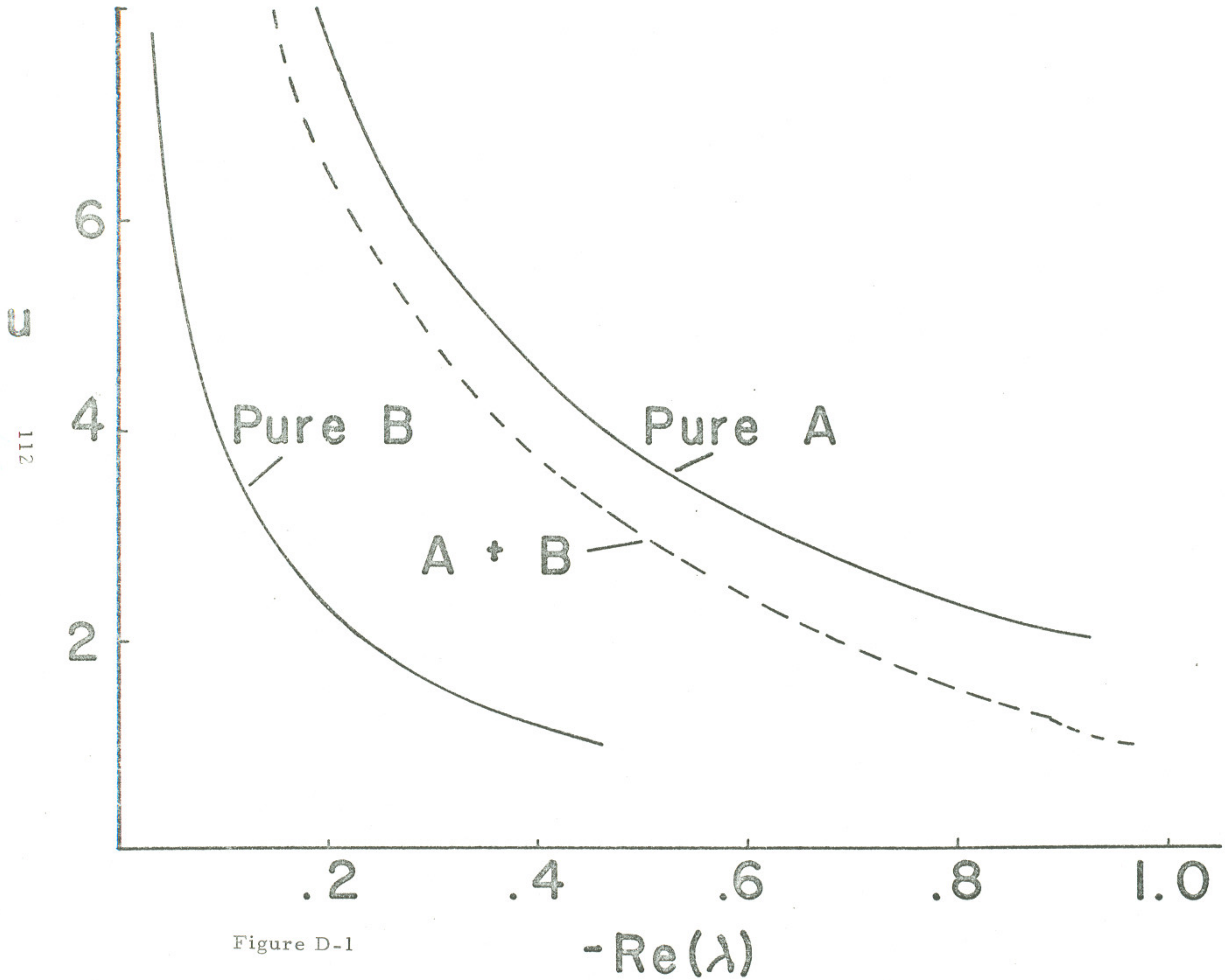


Figure D-1

$$2ue^{-2\lambda} = 2u + 2\lambda$$

or
$$ue^{-2\lambda} = u + \lambda \quad . \tag{D-4}$$

The λ of largest real part that is a solution of equation (D-4) will not be the same λ that was associated with equation (D-2). This is the curve labeled 'Pure B' in Figure D-1. Thus, when scaled to the A fluid parameters, pure A and pure B are different. The curve labeled 'A+B' is for a 50/50 mixture of A and B type fluids. Its equation, when scaled to the A fluid parameters, is

$$u(x_1 e^{-\lambda} + (1-x_1)e^{-2\lambda}) = u + \lambda \quad . \tag{D-5}$$

(this is for a mixture with hard-sphere diameter ratio equal to 2). When $x_1 \to 1$ equation (D-5) reduces to the pure A form and when $x_1 \to 0$ it reduces to the pure B form, exactly as it should since x_1 is the concentration of A.

Figure D-2 shows a plot of Im(λ) versus N for systems scaled to the N = 1 parameters.

The same type of considerations apply to the lattice gas systems. For example, consider the case MN = 3.

$$\frac{x_1(1-e^{-\xi a})e^{-max}}{1-e^{-\xi a}e^{-as}} + \frac{x_2(1-e^{-\xi a})e^{-mNas}}{1-e^{-\xi a}e^{-as}} = 0 \tag{D-6}$$

If we let $x_1 \to 1$, then $x_2 \to 0$ and we obtain,

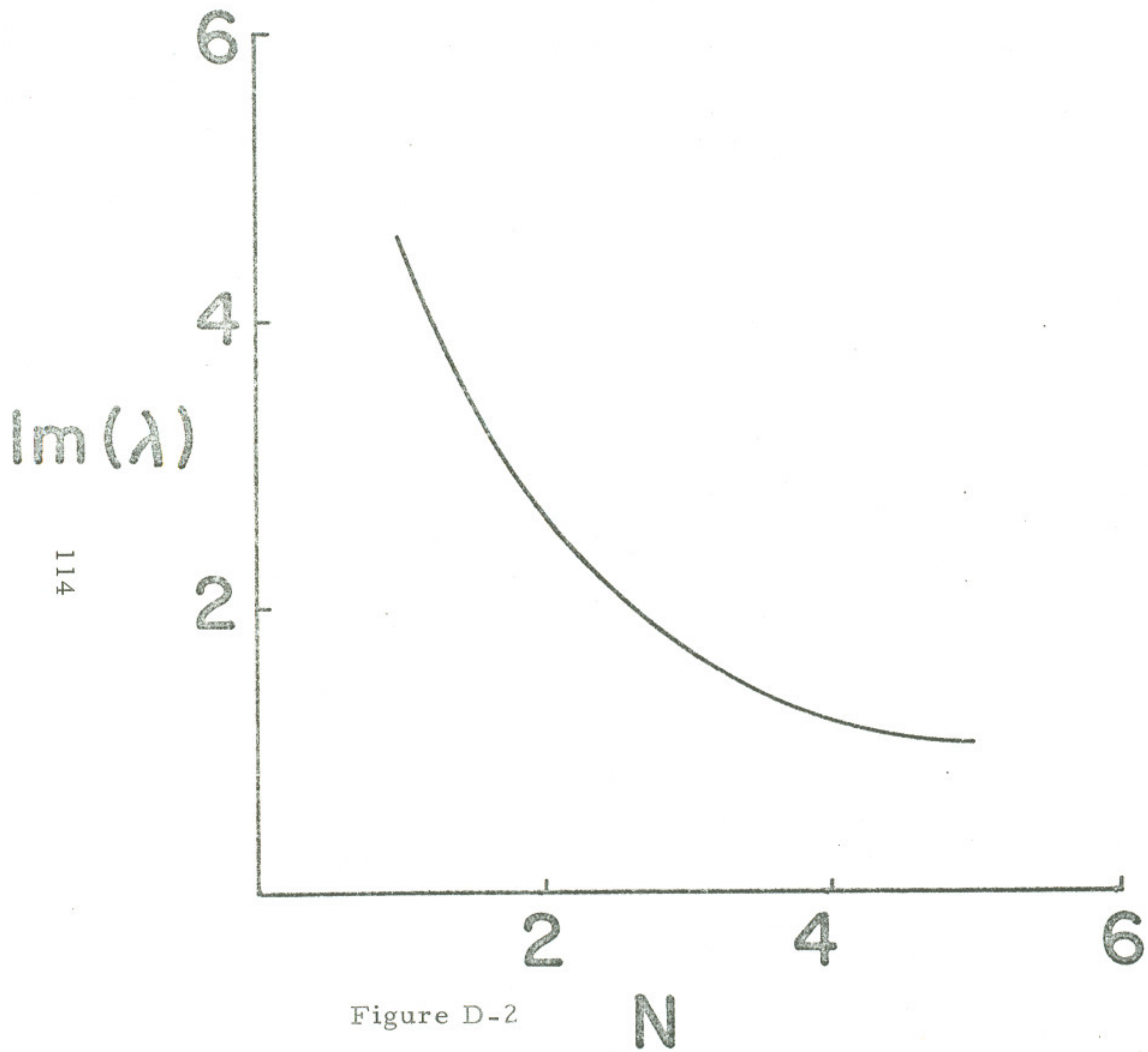


Figure D-2

$$\frac{(1-e^{-\xi a})\, e^{-max}}{1-e^{-\xi a}\, e^{-as}} = 0 \qquad \text{(D-7)}$$

If we let $x_1 \to 0$, the $x_2 \to 1$, and we obtain

$$\frac{(1-e^{-\xi a})\, e^{-mNas}}{1-e^{-\xi a}\, e^{-as}} = 0 \quad , \qquad \text{(D-8)}$$

but this is scaled to the A system, i.e. a system with hard-sphere diameter to lattice constant equal to M. If we scale everything to the B system we obtain

$$\frac{(1-e^{-\xi a})\, e^{-mas}}{1-e^{-\xi a}\, e^{-as}} = 0 \quad , \qquad \text{(D-9)}$$

since for this system the hard-sphere diameter is Nb.

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BIOGRAPHY

The author was born and raised in Azusa, California. From 1961 until 1965 he attended Azusa High School specializing in college preparatory courses and playing varsity tennis.

In June of 1965 the author was graduated from Azusa High and moved to Socorro, New Mexico to begin his college career at the New Mexico Institute of Mining and Technology. While at the Institute the author studied physics and mathematics, graduating with highest honors in June of 1969 with a Bachelor of Science degree in physics and electronics. The author financed his undergraduate career working as a research assistant doing non-nuclear naval ordnance research for the United States Army and Navy.

In September of 1969 the author moved to Beaverton, Oregon to attend the Oregon Graduate Center for Study and Research. In April of 1972 he received a Master of Science degree in Physics, and in August of 1973 a Doctor of Philosophy degree in Theoretical Physics.