

degeneracy would occur when possible. The question then arises whether the coupling of vibrational and electronic motion is large enough to produce a statically distorted geometry. The lack of refocusing in NiF₂ and CoF₂, where ³Π and ⁴Φ electronic states are expected, is interpreted to imply the absence of a polar com-

ponent in either species at 1300°K. While it is of course not possible on the basis of the present qualitative deflection experiments to discuss in detail Renner-Teller splittings of vibronic degeneracies, these experiments do show that no large static distortions occur in the thermally accessible states of NiF₂ and CoF₂.

Convergence of Fugacity Expansion and Bounds on Molecular Distributions for Mixtures*

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We have generalized the methods developed recently by Groeneveld and Penrose for a one-component system to obtain a lower bound on the domain of convergence of the Mayer fugacity expansion of the pressure,

$$p = \sum b_{11}, \dots, \iota_\omega \Pi z_\alpha^{\iota_\alpha},$$

where z_α is the fugacity of the α th component, $\alpha = 1, \dots, \omega$. This series is convergent for

$$\sum_{\alpha=1}^{\omega} |z_\alpha| \leq [\exp(1 + 2\Phi/kT)B]^{-1},$$

where

$$B = \{\max(\alpha, \beta)\} \int |\exp[-(kT)^{-1}\phi_{\alpha\beta}(r)] - 1| d\mathbf{r}$$

and where the interaction potential $\phi_{\alpha\beta}(r)$ of a pair of particles of Species α and β satisfies

$$\sum_{i < j \leq s} \phi_{\alpha i \alpha j}(|x_i - x_j|) \geq -s\Phi$$

for all α, x , and s . [For a positive interparticle potential, $\phi_{\alpha\beta}(r) \geq 0$, $\Phi = 0$.] Consequently the system remains in a single phase in this region. We have also generalized the inequalities of Lieb, Penrose, Lebowitz, and Percus to this case. For positive potentials upper (lower) bounds are gotten for the pressure and the distribution functions by expanding in a Taylor series up to terms of even (odd) total order in the fugacities.

I. INTRODUCTION

RECENTLY, several authors obtained some mathematically rigorous and physically interesting results for one component fluids. We refer first to the results of Groeneveld¹, Penrose², and Ruelle³ who obtained lower bounds on the radius of convergence of the Mayer fugacity expansion for the pressure and the distribution functions. This enabled them to establish a lower bound on the fugacity at which a phase transition may occur. A lower bound on the radius of convergence of the virial expansion was also obtained by Lebowitz and Penrose.⁴ Independently of this, Lieb⁵ established (for certain types of intermolecular potential) rigorous upper and lower bounds for the pressure and density (as functions of the fugacity). These inequalities were elucidated and extended by Penrose⁶ and Lebowitz and Percus.⁷ It is the purpose of this note

to generalize the above results to mixtures. The convergence of the fugacity expansion is considered in Sec. II and the inequalities in Sec. III.

II. CONVERGENCE OF THE FUGACITY EXPANSION

Consider an open system of ω molecular species at the respective fugacities z_σ ($\sigma = 1, 2, \dots, \omega$) whose molecules interact in pairs with potentials $\varphi_{\sigma_i \sigma_j}(|\mathbf{r}_i - \mathbf{r}_j|)$ between every two molecules of species σ_i and σ_j which are at positions $\mathbf{r}_i, \mathbf{r}_j$ in space. Suppose also the existence of an external potential $u_{\sigma_i}(\mathbf{r}_i)$ acting on each molecule of species σ_i at \mathbf{r}_i . Using a notation due to Penrose, we write $(\sigma_i, \mathbf{r}_i) \equiv \tau_i$, $\varphi_{\sigma_i \sigma_j}(\mathbf{r}_i, \mathbf{r}_j) \equiv \varphi(\tau_i, \tau_j)$ and $u_{\sigma_i}(\mathbf{r}_i) \equiv u(\tau_i)$. Using this and also denoting

$$e_N(\tau^N) \equiv e_N(\tau_1, \dots, \tau_N) \equiv \prod_{i < j \leq N} \exp[-\beta\varphi(\tau_i, \tau_j)] \quad (2.1)$$

$$z_{\sigma_i} \exp[-\beta u(\tau_i)] \equiv \exp[\gamma(\tau_i)], \quad (2.2)$$

one can express the grand partition function for the system in the concise form

$$\Xi = \sum_{N=0}^{\infty} (N!)^{-1} \int \dots \int \prod_{i=1}^N \exp[\gamma(\tau_i)] e_N(\tau_N) d\tau^N, \quad (2.3)$$

where $\int d\tau$ stands for the multiple "summation" $\sum_\sigma \int d\mathbf{r}$.

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¹ J. Groeneveld, *Phys. Letters* **3**, 50 (1962).

² O. Penrose, *J. Math. Phys.* **4**, 1312 (1963).

³ D. Ruelle, *Ann. Phys. (N.Y.)* **25**, 109 (1963).

⁴ J. L. Lebowitz and O. Penrose, *J. Math. Phys.* (to be published).

⁵ E. Lieb, *J. Math. Phys.* **4**, 671 (1963).

⁶ O. Penrose, *J. Math. Phys.* **4**, 1488 (1963).

⁷ J. L. Lebowitz and J. K. Percus, *J. Math. Phys.* **4**, 1495 (1963).

and more generally

$$\int \dots \int d\tau^N \equiv \int \dots \int d\tau_1 \dots d\tau_N$$

$$\equiv \sum_{\sigma_1, \dots, \sigma_N} \int \dots \int d\mathbf{r}_{\sigma_1} \dots d\mathbf{r}_{\sigma_N} \quad (2.4)$$

A similarly simple expression is obtained for the distribution function of k specified molecules of Species α_i at Position $\mathbf{x}_i (i=1, \dots, k)$. Writing $(\alpha_i, \mathbf{x}_i) \equiv \xi_i$ we have for the distribution function

$$n_k(\xi^k) \equiv n_k(\xi_1, \dots, \xi_k) = (\Xi)^{-1} \sum_N (N!)^{-1} \prod_{i=1}^N \exp[\gamma(\xi_i)]$$

$$\times \int \dots \int \prod_{j=1}^N \exp[\gamma(\tau_j)] e_{k+N}(\xi^k, \tau^N) d\tau^N. \quad (2.5)$$

In the above notation the grand partition function and the molecular distributions $n_k(\xi^k)$ are functionals of the two functions $\gamma(\xi)$ and $\varphi(\xi, \mathbf{n})$ and the functional dependence on γ and φ is of the same form as in the one-component case. Hence all the equations derived by Lebowitz and Percus⁵ for the functionals $\Xi[\gamma]$ and $n_k(\xi^k, [\gamma])$ in the single component case are also valid in the multicomponent case, when their notation is given the above interpretation. In particular, consider the functional Taylor expansion of the functionals $\log \Xi[\gamma]$ and $n_k(\xi^k, [\gamma])$ around the "point" $e^\gamma=0$. The Taylor expansion of any functional $F[e^\gamma]$ is defined as the Taylor expansion of the function $F(\theta) \equiv F[\theta e^\gamma]$ at $\theta=1$ around the origin $\theta=0$. Then

$$F[e^\gamma] = F(1) = \sum_{l=0}^{\infty} (l!)^{-1} \int \dots \int F^{(l)}(0)$$

$$\times \exp[\gamma(\tau_1)] \dots \exp[\gamma(\tau_l)] d\tau_1 \dots d\tau_l, \quad (2.6)$$

where the coefficients $F^{(l)}(0)$ do not contain the function γ . It should be noted that in every term of order l in this expansion there is implicit a summation over all species for each of the l molecules. Thus a term of order l is actually a summation over all partial orders l_1, \dots, l_ω which add up to the total order $l=l_1+\dots+l_\omega$. The appropriate Taylor expansions for the functionals $\log \Xi[\gamma]$ and $n_k(\xi^k, [\gamma])$ become power series in the z_α in the absence of an external field. We have then $\exp[\gamma(\tau)] = z_\alpha$ and the power series are of the form

$$\beta P = V^{-1} \log \Xi$$

$$= \sum_l (l!)^{-1} \int \dots \int z_{\sigma_1} \dots z_{\sigma_l} U_l(\tau_1, \dots, \tau_l) d\tau_1 \dots d\tau_l \quad (2.7)$$

$$\frac{n_s(\xi^s, [z])}{z_{\alpha_1} \dots z_{\alpha_s}}$$

$$= \sum_l (l!)^{-1} \int \dots \int z_{\sigma_1} \dots z_{\sigma_l} F_l(\xi^s; \tau_1, \dots, \tau_l) d\tau_1 \dots d\tau_l, \quad (2.8)$$

where V is volume of the container to which the system is confined and the U 's and the F 's have the same functional dependence on $\varphi(\tau_1, \tau_2)$ as the analogous coefficients in the one-component system have on $\varphi(\mathbf{r}_1, \mathbf{r}_2)$. More precisely $U_l(\tau_1, \dots, \tau_l)$ is the cluster function⁸ of the l molecules of the given species; also, $F_l(\xi^s, \tau_1, \dots, \tau_l)$ is the sum of cluster functions of the $l+s$ molecules of the given species, each of the clusters containing some of the s molecules.

Writing now

$$\int \dots \int U_l(\tau_1, \dots, \tau_l) d\mathbf{r}_1 \dots d\mathbf{r}_l = u(l_1, \dots, l_\omega) \quad (2.9)$$

and

$$\int \dots \int F_l(\xi^s; \tau_1, \dots, \tau_l) d\mathbf{r}_1 \dots d\mathbf{r}_l = F_l(\xi^s; l_1, \dots, l_\omega) \quad (2.10)$$

one obtains the power series⁸

$$\beta P(z, v) = \sum_{l_1, \dots, l_\omega} \frac{z_1^{l_1} \dots z_\omega^{l_\omega}}{l_1! \dots l_\omega!} u(l_1, \dots, l_\omega)$$

$$= \sum z_1^{l_1} \dots z_\omega^{l_\omega} b_{l_1, \dots, l_\omega} \quad (2.11)$$

$$\frac{\pi(\xi^s, [z])}{z_{\alpha_1} \dots z_{\alpha_s}} = \sum_{l_1, \dots, l_\omega} \frac{z_1^{l_1} \dots z_\omega^{l_\omega}}{l_1! \dots l_\omega!} F(\xi^s; l_1, \dots, l_\omega)$$

$$= \sum z_1^{l_1} \dots z_\omega^{l_\omega} a_{l_1, \dots, l_\omega}(\xi^s). \quad (2.12)$$

The b_{l_1, \dots, l_ω} are the multicomponent analogs of the cluster integrals b_l and similarly the $a_{l_1, \dots, l_\omega}(\xi^s)$ correspond to the coefficients $a_{s+l}(\mathbf{r}^s)$ in the one-component fugacity expansion of the distribution function $n_s(\mathbf{r}^s)$. $u(l_1, \dots, l_\omega)$ reduces to $u(l)$, ($l=l_1+\dots+l_\omega$) of the one-component case if the functions $\varphi_{\sigma_i \sigma_j}$ are all identical, and similarly for the F 's. Hence if there exist recurrence relations for upper or lower bounds of the $u(l)$'s or $F(l)$'s in the one-component case which are valid when any one of the potentials $\varphi_{\sigma \omega_j}$ are used in the $u(l)$'s [$F(l)$'s], then these bounds are also bounds of the $u(l_1, \dots, l_\omega)$'s, [$F(l)$'s]. This is so in the case of the bounds found by Groeneveld¹ and Penrose² for the $u(l)$'s and $F(l)$'s:

Penrose found the following upper bounds to the coefficients $b_l \equiv u(l)/l!$ in the one-component case,

$$|b_l| \leq \exp[2(l-2)\beta\Phi] [lB(V)]^{l-1}/l!, \quad (2.13)$$

where Φ is a constant satisfying

$$-\Phi \leq (1/s) \sum_{i < j \leq s} \varphi(\mathbf{x}_i, \mathbf{x}_j)$$

for every s and $\mathbf{x}_i, (i=1, \dots, s)$ and

$$B(V) = \max_{(x)} \int |f(|\mathbf{x} - \mathbf{y}|)| d\mathbf{y}$$

$$\{f(|\mathbf{x} - \mathbf{y}|) = \exp[-\beta\varphi(|\mathbf{x} - \mathbf{y}|)] - 1\},$$

where V is the volume of the container.

⁸ W. G. McMillan and J. E. Mayer, J. Chem. Phys. **13**, 276 (1945).

The above bounds become valid also for the $u(l_1, \dots, l_\omega)$ if we require

$$-\Phi \leq \sum_{i < j \leq s} \varphi_{\sigma_i \sigma_j}(\mathbf{x}_i, \mathbf{x}_j)$$

for every s, \mathbf{x}_i , and σ_i and

$$B(V) = \max_{(\alpha, \beta)} \int |f_{\alpha\beta}(|\mathbf{x} - \mathbf{y}|)| d\mathbf{y} \\ \{f_{\alpha\beta}(|\mathbf{x} - \mathbf{y}|) = \exp[-\beta\varphi_{\alpha\beta}(|\mathbf{x} - \mathbf{y}|)] - 1\}.$$

It follows that

$$u(l_1, \dots, l_\omega) \leq C_l \equiv \exp[2(l-2)\beta\Phi]^{l-2} B(V)^{l-1}$$

and that the power series for βP is majorized

$$\beta P = \sum_{l_1, \dots, l_\omega} (z_1^{l_1} \dots z_\omega^{l_\omega}) / (l_1! \dots l_\omega!) u(l_1, \dots, l_\omega) \\ \ll \sum_l (C_l/l!) (|z_1| + \dots + |z_\omega|)^l. \quad (2.14)$$

The latter series will necessarily converge in the range

$$|z_1| + \dots + |z_\omega| \leq \liminf (l!/C_l)^{1/l} \\ = [B(V) \exp(1+2\beta\Phi)]^{-1}. \quad (2.15)$$

The same result holds also for the series (2.12) for the distribution functions.

An argument used by Penrose in the one-component case may now be readily generalized to show that the thermodynamic pressure,

$$P^0(z_1, \dots, z_\omega) = \lim_{V \rightarrow \infty} P(z_1, \dots, z_\omega, V) \quad (2.16)$$

will be an analytic function of its arguments for

$$|z_1| + \dots + |z_\omega| < B \exp(1+2\beta\Phi), \quad (2.17)$$

where

$$B = \lim_{V \rightarrow \infty} B(V),$$

and will be given by

$$P^0(z_1, \dots, z_\omega) = \sum z_1^{l_1} \dots z_\omega^{l_\omega} b_{l_1, \dots, l_\omega}^0, \quad (2.18)$$

where

$$b_{l_1, \dots, l_\omega}^0 = \lim_{V \rightarrow \infty} b_{l_1, \dots, l_\omega}(V). \quad (2.19)$$

Hence in the domain of fugacities defined in (2.17) the system will be in a homogeneous gaseous phase, no phase transition of any kind having been able to occur.

For positive potentials, $\varphi(\tau_i, \tau_j) \geq 0$, $\Phi = 0$ and B is given by

$$B = \max_{(\alpha, \beta)} \left\{ - \int f_{\alpha\beta}(\mathbf{r}) d\mathbf{r} \right\}. \quad (2.20)$$

The integral in the parenthesis is just twice the second virial coefficient for a monatomic gas whose particles interact with a potential $\varphi_{\alpha\beta}(\mathbf{r})$.

III. INEQUALITIES

General inequalities for molecular distribution functions $n_k(\xi^k)$ in multicomponent systems can be obtained, as mentioned above, by reinterpreting all general equations and inequalities for the functionals

$n_k(\xi^k, [\gamma])$ in the single-component case. Following Lebowitz and Percus⁵ we write

$$n_{k+s}(\xi^k, \mathbf{n}^s, [\gamma]) / n_s(\mathbf{n}^s, [\gamma]) = n_k(\xi^k, [\gamma - \beta \sum_j \varphi_{\mathbf{n}_j}]). \quad (3.1)$$

as the expression for the conditional distribution function of the set of molecules (ξ^k) when the set (\mathbf{n}^s) of molecules is given. Here the sets are defined by

$$(\xi^k) \equiv (\xi_1, \dots, \xi_k), \quad (\xi_i) \equiv (\alpha_i, \mathbf{x}_i) \\ (\mathbf{n}^s) \equiv (\mathbf{n}_1, \dots, \mathbf{n}_s), \quad (\mathbf{n}_i) \equiv (\beta_i, \mathbf{y}_i) \quad (3.2)$$

and φ_{η_j} denotes the function (of a variable τ) $\varphi(\mathbf{n}_j, \tau)$. Furthermore, generally for every set (\mathbf{n}^s) we have

$$n_s(\mathbf{n}^s) = (\Xi[\gamma - \beta \sum_j \varphi_{\mathbf{n}_j}] / \Xi[\gamma]) \prod_j \exp[\gamma(\mathbf{n}_j)] e_s(\mathbf{n}^s) \quad (3.3)$$

and also

$$\Xi[\gamma - \beta \sum_j \varphi_{\mathbf{n}_j}] e_s(\mathbf{n}^s) \\ = \frac{\delta^s \Xi[\gamma]}{\delta \exp[\gamma(\mathbf{n}_1)] \dots \delta \exp[\gamma(\mathbf{n}_s)]}. \quad (3.4)$$

Defining now the functional

$$G_m(\xi^m, [e^\gamma]) \equiv \frac{\delta^m \Xi[\gamma]}{\delta \exp[\gamma(\xi_1)] \dots \delta \exp[\gamma(\xi_m)]} \quad (3.5)$$

and making use of (3.4) and (3.3), we can write (3.1) in the form

$$\frac{n_{k+s}(\xi^k, \mathbf{n}^s) \cdot e_k(\xi^k)}{\prod_j \exp[\gamma(\mathbf{n}_j)] \cdot e_{k+s}(\xi^k, \mathbf{n}^s)} \\ = \frac{\prod_i \exp[\gamma(\xi_i)]}{\Xi[\gamma]} G_k(\xi^k, [\exp\{\gamma - \beta \sum_j \varphi_{\eta_j}\}]). \quad (3.6)$$

We write now a Taylor expansion, with remainder, for the functional $G_k(\xi^k, [\exp\{\gamma - \beta \sum_j \varphi_{\eta_j}\}])$ around the "point" e^γ ; We define for a fixed θ the function

$$\exp[\gamma(\tau/\theta)] = \exp[\gamma(\tau)] + \theta \Delta \exp[\gamma(\tau)] \\ = \exp[\gamma(\tau)] (1 + \theta \{\exp[-\beta \sum_j \varphi_{\eta_j}(\tau)] - 1\}) \quad (3.7)$$

and the functional

$$G_k(\xi^k, \{\exp[\gamma(|\theta|)]\}) \equiv G_k(\xi^k | \theta).$$

We have then

$$G_k(\xi^k, [\exp\{\gamma - \beta \sum_j \varphi_{\mathbf{n}_j}\}]) \equiv G_k(\xi^k | 1) \\ = \sum_{j=0}^l (j!)^{-1} \int \dots \int \frac{\delta^j G_k(\xi^k, [\gamma])}{\delta \exp[\gamma(\tau_1)] \dots \delta \exp[\gamma(\tau_j)]} \\ \times \Delta \exp[\gamma(\tau_1)] \dots \Delta \exp[\gamma(\tau_j)] d\tau^j \\ + (l!)^{-1} \int_0^1 d\theta (1-\theta)^l \\ \times \int \dots \int \frac{\delta^{l+1} G_k[\gamma(|\theta|)]}{\delta \exp[\gamma(\tau_1 | \theta)] \dots \delta \exp[\gamma(\tau_{l+1} | \theta)]} \\ \times \Delta \exp[\gamma(\tau_1)] \dots \Delta \exp[\gamma(\tau_{l+1})] d\tau^{l+1}. \quad (3.8)$$

Inserting (3.8) into (3.6) we get the Lebowitz–Percus equation [Eq. (3.10), Ref. 5]

$$\frac{n_{k+s}(\xi^k, \mathbf{n}^s) e_k(\xi^k)}{e_{k+s}(\xi^k, \mathbf{n}^s) \prod_j \exp[\gamma(\mathbf{n}_j)]} = N_{k,s}^{(l)} + R_{k,s}^{(l)}(\xi^k, \mathbf{n}^s), \quad (3.9)$$

where $N_{k,s}^{(l)}(\xi^k, \mathbf{n}^s)$ contains the Taylor expansion up to the l th term and $R_{k,s}^{(l)}(\xi^k, \mathbf{n}^s)$ is the remainder. They are given by

$$N_{k,s}^{(l)}(\xi^k, \mathbf{n}^s) = \sum_{j=0}^l (j!)^{-1} \int \dots \int n_{k+j}(\xi^k, \boldsymbol{\tau}^j) \prod_{i=1}^j f(\mathbf{n}^s, \boldsymbol{\tau}_i) d\boldsymbol{\tau}^j \quad (3.10)$$

$$R_{k,s}^{(l)}(\xi^k, \mathbf{n}^s) = (l!)^{-1} \int_0^1 d\theta (1-\theta)^l \int \dots \int \prod_{i=1}^k \times \exp[\gamma(\xi_i) - \gamma(\xi_i | \theta)] \prod_{j=1}^{l+1} \exp[\gamma(\boldsymbol{\tau}_j) - \gamma(\boldsymbol{\tau}_j | \theta)] \times \frac{\Xi(\theta)}{\Xi(0)} n_{k+l+1}(\xi^k, \boldsymbol{\tau}^{l+1} | \theta) \prod_{i=1}^{l+1} f(\mathbf{n}^s, \boldsymbol{\tau}_i) d\boldsymbol{\tau}^{l+1}, \quad (3.11)$$

where

$$f(\mathbf{n}^s, \boldsymbol{\tau}) \equiv \exp[-\gamma(\boldsymbol{\tau})] \Delta e^\gamma = \exp[-\beta \sum_j \varphi_{\mathbf{n}_j}(\boldsymbol{\tau})] - 1. \quad (3.12)$$

In the case of positive potentials for all types of pairs, i.e., $\varphi_{\sigma_i \sigma_j}(|\mathbf{r}_i - \mathbf{r}_j|) \geq 0$ for all σ and \mathbf{r} , $f(\mathbf{n}^s, \boldsymbol{\tau})$ is negative for all $\boldsymbol{\tau}$ and one gets as in the single component case, a bound on the remainder

$$(-1)^{l+1} R_{k,s}^{(l)}(\xi^k, \mathbf{n}^s) \geq 0. \quad (3.13)$$

Furthermore, here also

$$dG_m(\xi^m | \theta) / d\theta \leq 0 \text{ and } G_m(\xi^m | 1) \leq G_m(\xi^m | \theta) \text{ for } 0 \leq \theta \leq 1$$

so that a stronger bound on the remainder is obtained by replacing $G_{k+l}(\theta)$ by $G_{k+l}(1)$ in the expression for remainder (3.11):

$$(-1)^{l+1} R_{k,s}^{(l)} \geq \frac{1}{(l+1)! \prod_j \exp[\gamma(\mathbf{n}_j)]} \times \int \dots \int n_{k+s+l+1}(\xi^k, \mathbf{n}^s, \boldsymbol{\tau}^{l+1}, [\gamma]) \times \frac{e_{k+l+1}(\xi^k, \boldsymbol{\tau}^{l+1})}{e_{k+s+l+1}(\xi^k, \mathbf{n}^s, \boldsymbol{\tau}^{l+1})} \prod_{i=1}^{l+1} f(\mathbf{n}^s, \boldsymbol{\tau}_i) d\boldsymbol{\tau}^{l+1}. \quad (3.14)$$

Finally explicit inequalities are now obtained by reinserting into the formulas the definitions of the symbols $\xi, \mathbf{n}, \boldsymbol{\tau}, \int d\boldsymbol{\tau}$. In the case of no external potential and assuming that the single particle distribution function is equal to the macroscopic particle density

one has from (3.9), (3.10), and (3.13);

$$\rho_\beta / z_\beta \leq 1 \quad (s=1, k=0, l=0), \quad (3.15)$$

$$\frac{\rho_\beta}{z_\beta} \geq 1 + \sum_\sigma \rho_\sigma \int f_{\beta\sigma}(|\mathbf{y}_\beta - \mathbf{r}_\sigma|) d\mathbf{r}_\sigma \quad (s=1, k=0, l=1), \quad (3.16)$$

$$\frac{n_{\alpha\beta}(\mathbf{x}_\alpha, \mathbf{y}_\beta)}{e_{\alpha\beta}(\mathbf{x}_\alpha, \mathbf{y}_\beta) z_\beta} \leq \rho_\alpha \quad (s=1, k=1, l=0), \quad (3.17)$$

$$\frac{n_{\alpha\beta}(\mathbf{x}_\alpha, \mathbf{y}_\beta)}{e_{\alpha\beta}(\mathbf{x}_\alpha, \mathbf{y}_\beta)} \geq \rho_\alpha + \sum_\sigma n_{\alpha\sigma}(\mathbf{x}_\alpha, \mathbf{r}_\sigma) f_{\beta\sigma}(|\mathbf{y}_\beta - \mathbf{r}_\sigma|) d\mathbf{r}_\sigma \quad (s=1, k=1, l=1), \text{ etc.} \quad (3.18)$$

From (3.15) and (3.16), bounds can be obtained on the ρ 's in terms of the z 's and vice versa:

$$z_\beta + z_\beta \sum_\sigma z_\sigma \int f_{\beta\sigma} d\mathbf{r}_\sigma \leq \rho_\beta \leq z_\beta \quad (3.19)$$

$$\rho_\beta \leq z_\beta \leq \rho_\beta / (1 + \sum_\sigma \rho_\sigma \int f_{\beta\sigma} d\mathbf{r}_\sigma) \quad (\text{Provided the denominator is positive}) \quad (3.20)$$

The inequalities (3.15) and (3.16) can also be considered as bounds on each ρ_β in terms of z_β and the other ρ 's:

$$z_\beta (1 + \sum_{\sigma \neq \beta} \rho_\sigma \int f_{\beta\sigma} d\mathbf{r}_\sigma) / (1 - z_\beta \int f_{\beta\beta} d\mathbf{r}_\beta) \leq \rho_\beta \leq z_\beta. \quad (3.21)$$

A whole set of inequalities—Lieb's inequalities³—in terms of the ρ 's and z 's can be obtained from the above set for the singlet distribution $n_1(\mathbf{n})$ (with $k=0, s=1, l=1, 2, 3, \dots$) by elimination of the higher molecular distribution functions by successive substitutions from the appropriate inequalities (with $k=1, 2, \dots$). For example, one has (with $k=0, s=1, l=2$)

$$\frac{\rho_\beta}{z_\beta} \leq 1 + \sum_\sigma \rho_\sigma \int f_{\beta\sigma} d\mathbf{r}_\sigma + (2!)^{-1} \sum_{\sigma_1 \sigma_2} \iint n_{\sigma_1 \sigma_2}(\mathbf{r}_{\sigma_1}, \mathbf{r}_{\sigma_2}) f_{\beta\sigma_1} f_{\beta\sigma_2} d\mathbf{r}_{\sigma_1} d\mathbf{r}_{\sigma_2} \quad (3.22)$$

and (3.17) can be used to eliminate the pair distribution from the right hand side of (3.22) to give

$$\frac{\rho_\beta}{z_\beta} \leq 1 + \sum_\sigma \rho_\sigma \int f_{\beta\sigma} d\mathbf{r}_\sigma + \frac{1}{2} \sum_{\sigma_1 \sigma_2} \rho_{\sigma_1} z_{\sigma_2} \int f_{\beta\sigma_1} f_{\beta\sigma_2} e_{\sigma_1 \sigma_2}(\mathbf{r}_{\sigma_1}, \mathbf{r}_{\sigma_2}) d\mathbf{r}_{\sigma_1} d\mathbf{r}_{\sigma_2}. \quad (3.23)$$

The general inequalities are of the form

$$(-1)^l \rho_\alpha \leq (-1)^l \times \{z_\alpha + \sum_\sigma \rho_\sigma \sum_{\nu_1 + \dots + \nu_\omega \leq l} a_{\nu_1 \dots \nu_\omega}^{(\sigma, \alpha)} z_1^{\nu_1} \dots z_\omega^{\nu_\omega}\} \quad (3.24)$$

with coefficients $a_{\nu_1 \dots \nu_\omega}^{(\sigma, \alpha)}$ independent of l . These general inequalities can be derived by closely following

Penrose's method⁴ of examining the properties (alternating sign) of the remainders in the power expansions of the distribution functions. The coefficients $a_{\nu_1 \dots \nu_\omega}^{(\sigma, \alpha)}$ can now be found in terms of the coefficients of the fugacity expansions of the ρ 's, by going over to the limit $l = \infty$ in (3.24), substituting the expansions for the ρ 's and equating coefficients. By a similar process of elimination, inequalities can be obtained for ρ_α in terms of the z 's alone, where now the coefficients in the inequalities are simply the coefficients of the fugacity expansion. We have

$$(-1)^{l+1} \rho_\alpha \leq (-1)^{l+1} \sum_{\nu_1 + \dots + \nu_\omega \leq l} \nu_\alpha b_{\nu_1 \dots \nu_\omega} z_1^{\nu_1} \dots z_\omega^{\nu_\omega}. \quad (3.25)$$

Also, since

$$P = \int_{(0, \dots, 0)}^{(z_1, \dots, z_\omega)} \sum_\alpha \frac{\rho_\alpha}{z_\alpha} dz_\alpha \quad (3.26)$$

(where the integration is along any path in the ω -dimensional space $[z_1, \dots, z_\omega]$), we have

$$(-1)^{l+1} p \leq (-1)^{l+1} \sum_{\nu_1 + \dots + \nu_\omega \leq l} b_{\nu_1 \dots \nu_\omega} z_1^{\nu_1} \dots z_\omega^{\nu_\omega}. \quad (3.27)$$

In the case of more general potentials, the inequalities in the one-component case can again be extended to the multicomponent case by requiring the existence of a bound (hard-core assumption)

$$-\Phi' \leq \sum_{j=1}^s \varphi_{\alpha\sigma_j} (|\mathbf{x} - \mathbf{r}_j|) \quad (3.28)$$

for every α, σ , and s and all positions \mathbf{x}, \mathbf{r}_j , for which the Boltzman factor $e_{s+1}(\mathbf{x}, \mathbf{r}_1, \dots, \mathbf{r}_s)$ does not vanish. We have then always

$$\Xi[\gamma - \beta \sum_{j=1}^s \varphi_{\mathbf{n}_j}] \leq \Xi[\gamma] \exp(s\beta\Phi') \quad (3.29)$$

$$\begin{aligned} \Xi[\gamma - \beta \sum_j \varphi_{\mathbf{n}_j}] \cdot n_k(\xi^k, [\gamma - \beta \sum_j \varphi_{\mathbf{n}_j}]) &\leq n_k(\xi^k, [\gamma]) \\ &\times \exp(s\beta\Phi') \Xi[\gamma] \cdot [e_{k+s}(\xi^k, \mathbf{n}^s) / e_k(\xi^k) e_s(\mathbf{n}^s)] \end{aligned} \quad (3.30)$$

and applying these inequalities to (3.1) and (3.3) we have

$$\frac{n_{k+s}(\xi^k, \mathbf{n}^s)}{e_{k+s}(\xi^k, \mathbf{n}^s)} \leq \frac{n_s(\mathbf{n}^s)}{e_k(\xi^k)} \exp(s\beta\Phi'), \quad (3.31)$$

and in particular,

$$\rho_\alpha / z_\alpha \leq \exp(\beta\Phi'). \quad (3.32)$$

Also, the method^{4,5} used to split the remainder $R_{k,s}^{(l)}$ in (3.9) into a positive and negative term by splitting the function $f(\mathbf{r}) = \exp[-\beta\varphi(\mathbf{r})] - 1$ into a difference

of two nonnegative functions $f^+(\mathbf{r})$ and $f^-(\mathbf{r})$ is independent of the type of variable (\mathbf{r}) and hence applies also in the multicomponent case. By defining

$$\begin{aligned} f^+(\mathbf{n}, \boldsymbol{\tau}) &= \max\{0; f(\mathbf{n}, \boldsymbol{\tau})\}; \\ f^-(\mathbf{n}, \boldsymbol{\tau}) &= \min\{0; f(\mathbf{n}, \boldsymbol{\tau})\} \end{aligned} \quad (3.33)$$

we have (with $k=0, s=1, l=1$)

$$\frac{\rho_\beta}{z_\beta} \leq 1 + \exp(\beta\Phi') \sum_\sigma \rho_\sigma \int f_{\sigma\beta}^+ d\mathbf{r}_\sigma, \quad (3.34)$$

$$\frac{\rho_\beta}{z_\beta} \geq 1 - \exp(\beta\Phi') \sum_\sigma \rho_\sigma \int f_{\sigma\beta}^- d\mathbf{r}_\sigma, \quad \text{etc.} \quad (3.35)$$

IV. DISCUSSION

We have shown in this paper the existence of a domain of fugacities

$$\sum_\alpha z_\alpha \leq [B(V) \exp(1+2\beta\Phi)]^{-1} \quad (4.1)$$

in which the Mayer fugacity series for the pressure and distribution functions of a mixture converge. It follows from this that the system will remain in a homogeneous gaseous phase even when $V \rightarrow \infty$ for the range of z_α 's satisfying the condition

$$\begin{aligned} \sum_\alpha z_\alpha &< \lim_{V \rightarrow \infty} [B(V) \exp(1+2\beta\Phi)]^{-1} \\ &= [B \exp(1+2\beta\Phi)]^{-1}. \end{aligned} \quad (4.2)$$

Equation (4.2) may be combined with the inequalities derived in Sec. III to obtain a lower bound on the densities at which a phase transition may occur. Thus combining (3.35) with (4.2) yields for this domain of densities

$$\begin{aligned} \sum_\alpha [\rho_\alpha / (1 - \exp(2\beta\Phi) \sum_\sigma \rho_\sigma \int f_{\sigma\alpha}^- d\mathbf{r}_\sigma)] \\ \leq [B \exp(1+2\beta\Phi)]^{-1}. \end{aligned} \quad (4.3)$$

For the case of positive potentials (4.3) becomes

$$\sum_\alpha [\rho_\alpha / (1 + 2 \sum_\sigma b_{\alpha\sigma} \rho_\sigma)] < B. \quad (4.4)$$

It should be noted here that all our results for infinite systems require the existence of the limit in (4.2). They do not thus apply to plasmas or ionic mixtures even if the short-range part of the potential is correctly taken into account. This is not surprising since, as is well known, the densities are not analytic in the fugacities at $z_\alpha = 0$ in the limit $V \rightarrow \infty$.