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Inverse Problem in Classical Statistical Mechanics*

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Examples of inverse solutions for the effective additive pair potential from guessed equilibrium pair distribution are given for the Percus-Yevick, hypernetted-chain, and Stillinger-Buff (with an inexact mean-density closure relation) equations. The found potentials depend on density and temperature and the potential for a given guessed distribution predicted by the Percus-Yevick theory is always smaller than that from the hypernetted chain equation. The exact inverse problem of determining the potential from the nonuniform pair distribution is formulated via the Stillinger-Buff equation and the difficulties in solving this problem are indicated. In a related inverse problem we characterize the possible equations of state consistent with the assumption that the potential of mean force of the fluid is directly proportional to the, possibly density dependent, pair potential.

1. INTRODUCTION

If the direct problem of statistical mechanics consists in finding the macroscopic properties of matter given the molecular interaction, an inverse problem may be formulated: given the macroscopic properties and relations connecting these to the molecular interaction, what interactions are consistent with the given information. For example, Frisch and Helfand[1] and Keller and Zumino[2] showed that, restricting the class of potentials to monotone increasing or decreasing, pairwise additive and central, the second virial coefficient, in the virial expansion of the pressure, given as a function of temperature, T, $(0 \leqslant T < \infty)$ uniquely determines the intermolecular potential function.

In this paper we shall be concerned also with a different inverse problem: It consists of picking a molecular distribution function for a pair (or triplet) of molecules and determining the pair intermolecular potential which could give rise to this molecular distribution function. Functional derivative techniques applied to the grand canonical-coordinate distributions provide several connecting relationships, approximate and exact, for potential and molecular distribution function. Among these the inexact Percus-Yevick (PY) and convolution hypernetted-chain (CHNC) equations employing a guessed pair distribution function and the exact Stillinger-Buff equations (employing a guessed triplet distribution function) allow easy separability of the pair intermolecular potential. Once a corresponding solution pair, pair potential-pair distribution function, has been obtained by this procedure the equations of state can be found either by the virial or compressibility relation.

Before we turn to the inverse solution of the PY and CHNC equations which are discussed in Sec. 2 we would like to point out that, in general, an inverse solution for a pair potential from a hypothetical, guessed molecular distribution function may yield a pair intermolecular potential which will be a function not only of the intermolecular distances but also of the uniform density and temperature of the fluid. It is not astonishing to find that this is so even if the guessed molecular distribution function is exact and the exact Stillinger-Buff relations are employed. It will thus be necessary to comment shortly on the validity of the fundamental relations employed, e.g., the PY equation, etc., for the case that the intermolecular potential is a function of the uniform density, ρ, and temperature, T. When an effective pair-wise additive potential Φ is determined for a real fluid from experimental x-ray scattering functions (structure functions), one finds a ρ, T dependence in Φ, arising from at least three causes, which should be sharply differentiated: (1) A spurious ρ, T dependence due to the use of an inexact equation relating the scattering function (i.e., essentially the Fourier transform of the pair distribution function minus one) and the sought-after pair potential, e.g., the use of the PY equation. (2) A second spurious ρ, T dependence of Φ which arises from a small experimental error in the measured scattering function. In Sec. 2 of this paper we will give an estimate of this effect. (3) Since all real molecules are polarizable there will always be a possibly small but real ρ, T dependence of Φ due to the nonpairwise electrical forces between them. Furthermore in systems containing charged particles, ions or electrons, there will be an appreciable ρ, T dependence due to screened long-ranged electrostatic interactions. Because of this, we investigate in Sec. 2 in some detail the inverse solution of the inexact PY (or CHNC) equation for a model system which reduces asymptotically for large distances to the Debye-Hückel screened Coulomb potential of a set of identical charged particles in a neutralizing background. By a small modification of this model one is able to mimic the behavior of the oscillating long-range part of the effective interatomic potential in a liquid metal.

In Sec. 3 we turn to the exact Stillinger-Buff equation. The exact inverse problem is difficult – to obtain an exact pair potential the guessed triplet distribution function must satisfy certain necessary and sufficient conditions to insure that it arises from some many-particle phase-space density. The technique may still be useful though for obtaining approximate solutions to many-body problems (an example is worked out), by requiring some limited consistency between the chosen triplet and the lower-order molecular distribution functions.

In the last section we turn to a different problem which is also an inverse problem. Given that we can prescribe the functional dependence of the pair distribution on Φ, what equation of state is consistent with this prescription? We examine a particularly simple case of this problem.

2. PY AND CHNC EQUATIONS

One can derive the PY and CHNC approximate integral equations for the pair distribution function by methods of functional differentiation[3]:

$$g(\vec{x})-1=c(\vec{x})+\rho\int c(\vec{x}-\vec{x}')[g(\vec{x}')-1]\,d\vec{x}', \tag{2.1}$$

$$c(\vec{x})=[1-e^{\beta\Phi(\vec{x})}]g(\vec{x})\qquad(\mathrm{PY}), \tag{2.2}$$

$$c(\vec{x})=g(\vec{x})-1-\ln g(\vec{x})-\beta\Phi(\vec{x})\qquad(\mathrm{CHNC}), \tag{2.3}$$

where $c(\vec{x})$ is the direct correlation function, $g(\vec{x})$ the pair distribution, and $\Phi(\vec{x})$ the pair potential. Equation (2.1) relating c and g as reciprocal kernels is exact while (2.2) and (2.3) are approximations. Even if the potential depends on the uniform density ρ and "temperature" $\beta=1/kT$, Eqs. (2.1)–(2.3) hold with ρ and β regarded then as parameters throughout the derivation. The compressibility relation for the thermodynamics, which is also derivable by functional differentiation,[4] is not changed when the potential depends on density and temperature, but the virial equation must be modified as we see later.

It is easy to express Φ as a functional of g (or $g-1=h$, the "indirect correlation function") by taking Fourier transforms:

$$\beta\Phi(\vec{x})=\ln\left(1-\frac{1}{1+h(\vec{x})}\frac{1}{(2\pi)^3}\int e^{i\vec{k}\cdot\vec{x}}\frac{\tilde{h}(\vec{k})}{1+\rho\tilde{h}(\vec{k})}\,d\vec{k}\right)\quad(\mathrm{PY}) \tag{2.4}$$

and

$$\beta\Phi=-\ln[1+h(\vec{x})]+h(\vec{x})-\frac{1}{(2\pi)^3}\int e^{i\vec{k}\cdot\vec{x}}\frac{\tilde{h}(\vec{k})}{1+\rho\tilde{h}(\vec{k})}\,d\vec{k}\quad(\mathrm{CHNC}) \tag{2.5}$$

with $\tilde{h}(\vec{k})=\int e^{-i\vec{k}\cdot\vec{x}}h(\vec{x})\,d\vec{x}$, and the integral term appearing in (2.4) and (2.5) being just the direct (pair) correlation function.

From (2.4) and (2.5) we see that the difference in pair potential $\Delta(\beta\Phi)=(\beta\Phi)_{\mathrm{PY}}-(\beta\Phi)_{\mathrm{CHNC}}$ is simply expressible as a function of $h(\vec{x})-c(\vec{x})$,

$$\Delta[\beta\Phi(\vec{x},\rho,\beta)]=\ln[1+h(\vec{x})-c(\vec{x})]-[h(\vec{x})-c(\vec{x})]. \tag{2.6}$$

The right-hand side of (2.6) is convex downward in the $h-c$ difference and achieves its minimum value of zero for the ideal gas or, in general, when $|\vec{x}|=r\to\infty$. Thus $\Delta(\beta\Phi)\leq 0$. It also follows that once an inverse solution of either (2.4) or (2.5) is obtained, the solution of the remaining equation can be obtained without further quadratures, using (2.6). One can also obtain $\Delta(\beta\Phi)$ directly from a measured scattering function, $S(\vec{k})$,[5]

$$S(\vec{k})=1+\rho\tilde{h}(\vec{k}), \tag{2.7}$$

the desired formula being

$$\Delta[\beta\Phi(\vec{x},\rho,\beta)]=-\ln\left(1-\frac{1}{(2\pi)^3\rho}\int e^{i\vec{k}\cdot\vec{x}}\frac{[S(\vec{k})-1]^2}{S(\vec{k})}\,d\vec{k}\right)-\frac{1}{(2\pi)^3\rho}\int e^{i\vec{k}\cdot\vec{x}}\frac{[S(\vec{k})-1]^2}{S(\vec{k})}\,d\vec{k}. \tag{2.8}$$

We now turn to the estimate of the error made in obtaining $\beta\Phi$ by employing say the PY Eq. (2.4) and the measured $S(\vec{k})$[6] subject to a small experimental error $\epsilon\delta S(\vec{k})$. Let the accurate value of S be $S_0(\vec{k})$ to which corresponds $h_0(\vec{x})$ via (2.7) and a $\beta\Phi_0(\vec{x}, \rho, \beta)$ via (2.4), we then set

$$S(\vec{k}) = S_0(\vec{k}) + \epsilon\,\delta S(\vec{k}), \quad h(\vec{x}) = h_0(\vec{x}) + \epsilon\,\delta h(\vec{x}), \quad \beta\Phi(\vec{x}) = \beta\Phi_0(\vec{x}) + \epsilon\beta\delta\Phi(\vec{x}). \tag{2.9}$$

Substituting (2.9) into (2.4) and solving for the error in $\beta\Phi$, $\beta\delta\Phi$, neglecting terms second order or higher in ϵ, we obtain

$$\beta\delta\Phi(\vec{x}) = \frac{e^{-\beta\Phi_0(\vec{x})}}{1+h_0(\vec{x})}\,\frac{1}{(2\pi)^3\rho}\left([1-e^{\beta\Phi_0(\vec{x})}]\int e^{i\vec{k}\cdot\vec{x}}\delta S(\vec{k})d\vec{k} - \int e^{i\vec{k}\cdot\vec{x}}\frac{\delta S(\vec{k})}{S_0{}^2(\vec{k})}d\vec{k}\right)$$

$$= \frac{e^{-\beta\Phi(\vec{x})}}{1+h(\vec{x})}\,\frac{1}{(2\pi)^3\rho}\left([1-e^{\beta\Phi(\vec{x})}]\int e^{i\vec{k}\cdot\vec{x}}\,\delta S(\vec{k})d\vec{k} - \int e^{i\vec{k}\cdot\vec{x}}\,\frac{\delta S(\vec{k})}{S^2(\vec{k})}d\vec{k}\right) + O(\epsilon). \tag{2.10}$$

A similar formula can be obtained for the CHNC equation. These formulas would allow one to remove the errors of type (2) mentioned in the introduction.

We now turn to some examples of inverse solutions of (2.4) and (2.5). Choosing,

$$h(\vec{x}) = [A(\rho, \beta)/r]\,e^{-B(\rho, \beta)r}, \tag{2.11}$$

where B is taken as positive and A is positive or negative such that $B^2 > 4\pi|A|\rho$. Substituting (2.11) in (2.4) and (2.5) yields

$$\beta\Phi(\vec{x}, \rho, \beta) = \ln\left[1 - \left(1+\frac{A}{r}e^{-Br}\right)^{-1}\frac{A}{r}e^{-(B^2+4\pi A\rho)^{1/2}r}\right] \quad \text{(PY)} \tag{2.12}$$

and
$$\beta\Phi(\vec{x}, \rho, \beta) = \ln\left(1+\frac{A}{r}e^{-Br}\right) + \frac{A}{r}e^{-Br} - \frac{A}{r}e^{-(B^2+4\pi A\rho)^{1/2}r} \quad \text{(CHNC)} \tag{2.13}$$

with
$$\beta\Phi(\vec{x}, 0, \beta) = -\ln\{1 + [A(0, \beta)/r]\,e^{-B(0, \beta)r}\} \tag{2.14}$$

at zero density for both. Consider now a set of charged particles, charge e, in a neutralizing background of dielectric constant ϵ. We can identify (2.11) with the familiar Debye-Hückel result if we choose $B^2 = 4\pi e^2\rho/\epsilon$. Asymptotically, for large r, (2.12) and (2.13) reduce to a shielded Coulomb potential. In particular, the shielding can be made to vanish if $B^2 = -4\pi A\rho$, $A < 0$, but then $\beta\Phi$ becomes imaginary as $r \to 0$.

Alternatively, one can interpret (2.11) as the PY or CHNC correlation function of *neutral* molecules satisfying the ρ, T dependent pair potentials (2.12) or (2.13), respectively. The compressibility relation, with $X = \beta p$, p the pressure, has the same form as when Φ is ρ, T independent,

$$\partial\rho/\partial X = 1 + \rho\int[g(\vec{x}) - 1]d\vec{x} = [1 - \rho\int c(\vec{x})d\vec{x}]^{-1} \tag{2.15}$$

and can be expressed in terms of the functions A and B appearing in (2.11), namely

$$\partial\rho/\partial X = B^2/(B^2 + 4\pi A\rho). \tag{2.16}$$

This compressibility equation of state will differ[7] in general from that obtained from the virial equation of state, which for ρ, T dependent potentials has the form

$$X = \rho - \tfrac{1}{6}\rho^2\int r[\partial(\beta\Phi)/\partial r]g(\vec{x})d\vec{x} + \tfrac{1}{2}\rho^3\int[\partial(\beta\Phi)/\partial r]g(\vec{x})d\vec{x}. \tag{2.17}$$

An oscillatory factor can be included in (2.11):

$$h(\vec{x}) = A(\rho, \beta)\exp[-B(\rho, \beta)r]\sin[C(\rho, \beta)r]/r\,, \tag{2.18}$$

resulting in

$$\beta\Phi(\vec{x}, \rho, \beta) = \ln\Bigg[1 - \left(1 + \frac{Ae^{-Br}}{r}\sin Cr\right)^{-1}$$

$$\times\frac{1}{2}\,\frac{ABC}{k_1{}^2+k_2{}^2}\,e^{-|k_2|r}\left(\left|\frac{k_2}{k_1}\right|\sin(|k_1|r) + \cos(|k_1|r)\right)\Bigg] \quad \text{(PY)} \tag{2.19}$$

and

$$\beta\Phi(\vec{x}, \rho, \beta) = -\ln\left(1 + \frac{Ae^{-Br}}{r}\sin Cr\right) + \frac{Ae^{-Br}}{r}\sin Cr$$

$$-\frac{1}{2}\frac{ABC}{k_1^2+k_2^2}\frac{e^{-|k_2|r}}{r}\left(\left|\frac{k_2}{k_1}\right|\sin(|k_1|r)+\cos(|k_1|r)\right)\quad \text{(CHNC)} \tag{2.20}$$

with $k_2=\pm\{\frac{1}{2}[(C^2-B^2)^2+4B^2C^2+8\pi A\rho CB]^{1/2}-\frac{1}{2}(C^2-B^2)\}^{1/2}$

and $k_1=\pm(C^2B^2+2\pi A\rho CB)^{1/2}/k_2.$

For large distances $\beta\Phi$ has the same form as $h(\vec{x})$, apart from scale and phase changes. The direct correlation functions [compare (2.1)] in these examples are identical for both approximate theories. Our interest in (2.18)–(2.20) arises from the fact that the large r asymptotic forms of (2.19) and (2.20) resemble the oscillating long-range part of the effective pair potential in a simple liquid metal (see, e.g., Ref. 5, Chap. 4), except that our asymptotic $\beta\Phi$ must be divided by r^2.

3. THE STILLINGER-BUFF EQUATION

The exact Stillinger-Buff equation[8] relates the pair potential to two-and three-particle distributions,

$$\beta\Phi(\vec{x}_{01})=-\ln g(\vec{x}_{01})+\int_0^\rho\int d\rho' d\vec{x}_2[g(\vec{x}_{02},\rho)c_n(\vec{x}_1,\vec{x}_2|\vec{x}_0;\rho')-c(\vec{x}_{12},\rho')]. \tag{3.1}$$

The nonuniform direct pair correlation between Molecules 1 and 2 given that there is a fixed molecule of the *same* kind at $\vec{x}_0$, $c_n(\vec{x}_1,\vec{x}_2|\vec{x}_0;\rho)$, is a solution of the nonuniform version of (2.1)

$$g_n(\vec{x}_1,\vec{x}_2|\vec{x}_0;\rho)-1=c_n(\vec{x}_1,\vec{x}_2|\vec{x}_0;\rho)+\rho\int c_n(\vec{x}_1,\vec{x}_3|\vec{x}_0;\rho)g(\vec{x}_{03})[g_n(\vec{x}_3,\vec{x}_2|\vec{x}_0;\rho)-1]d\vec{x}_3, \tag{3.2}$$

with the nonuniform pair function $g_n(\vec{x}_1,\vec{x}_2|\vec{x}_0;\rho)$ defined in terms of the uniform triplet distribution $g_3(\vec{x}_1,\vec{x}_2,\vec{x}_0;\rho)$ as follows:

$$g_n(\vec{x}_1,\vec{x}_2|\vec{x}_0;\rho)=g_3(\vec{x}_1,\vec{x}_2,\vec{x}_0;\rho/g(\vec{x}_{01})g(\vec{x}_{02}). \tag{3.3}$$

Equation (3.1) can be derived by functional differentiation and remains true for density and temperature dependent potentials. In principle, if one can guess a $c_n(\vec{x}_1,\vec{x}_2|\vec{x}_0;\rho)$ which can be derived from a positive, symmetric N-particle phase-space density, then substitution of this c_n in (3.1) assigns an exact $\beta\Phi$ which could give rise to this c_n. One necessary condition on c_n being that

$$\lim c_n(\vec{x}_1,\vec{x}_2|\vec{x}_0;\rho)=c(\vec{x}_{12};\rho),\quad |\vec{x}_0|\to\infty,\quad \vec{x}_1,\vec{x}_2 \text{ fixed,} \tag{3.4}$$

with $c(\vec{x}_{12};\rho)$ the uniform direct correlation function, from which $g(\vec{x}_{12})$ can be obtained through the Fourier transform of (2.1)

$$\tilde{h}(\vec{k})=\tilde{c}(\vec{k})/[1-\rho\tilde{c}(\vec{k})]. \tag{3.5}$$

Unfortunately, a useful characterization of the class of c_n which arise from a many-particle phase-space density is not at hand. One can still attempt to find an approximate $\beta\Phi$ using (3.1), by substituting in (3.1) an *inexact*, physically reasonable, guessed c_n satisfying (3.4). Such a c_n satisfying (3.4) will not, in general, satisfy all the marginal consistency conditions relating it to the lower, uniform two- and one-particle densities. Stillinger and Buff[8] have suggested that c_n acts like a uniform direct correlation function between molecules at $\vec{x}_1$ and $\vec{x}_2$, evaluated at an effective density, $\rho g(r_m,\rho)$ with $r_m=|\vec{x}_0-\frac{1}{2}(\vec{x}_1+\vec{x}_2)|$, namely,

$$c_n(\vec{x}_1,\vec{x}_2|\vec{x}_0;\rho)=c[\vec{x}_{12};\rho g(r_m,\rho)], \tag{3.6}$$

which satisfies (3.4). It would be of interest to carry through analytically an example of an approximate inverse solution of (3.1), subject to a closure relation such as the ansatz (3.6), for $\beta\Phi$ for the case where h is given by (2.11), for which the inverse PY and CHNC $\beta\Phi$ is easily obtained [compare (2.12) and (2.13)]. For this guessed form of h, the direct correlation is

$$c(r,\rho)=A(\rho,\beta)e^{-b(\rho,\beta)r}/r,\quad r=|\vec{x}_{12}|, \tag{3.7}$$

with $b^2(\rho,\beta)=B^2(\rho,\beta)+4\pi A(\rho,\beta)\rho.$

To proceed requires further mathematical simplification. We expand, compare (3.6) and (3.7), the functions A and b in (3.7),

$$\begin{aligned}A(\rho g(r_m),\beta)&=A(\rho+\rho h(r_m),\beta)=A(\rho,\beta)+(\partial A/\partial\rho)\rho h(r_m)+\cdots,\\ b(\rho g(r_m),\beta)&=b(\rho,\beta)+(\partial b/\partial\rho)\rho h(r_m)+\cdots,\end{aligned} \tag{3.8}$$

and replace $h(r_m)$ in (3.8) by an effective correlation given by a step function $h_0\theta(r_m,R)$ with

$$\theta(r_m, R) = 0, \quad r_m > R; \quad \text{or } 1, \quad r_m < R, \tag{3.9}$$

where the range R can be made to correspond to that of h as given by (2.11), $R = B^{-1}$ and h_0 can be chosen by the normalization requirement that [compare (2.16)]

$$\partial\rho/\partial X = B^2/(B^2 + 4\pi A\rho) = 1 + \tfrac{4}{3}\pi\rho h_0 R^3 . \tag{3.10}$$

Thus we replace the "midpoint-density" ansatz (3.6) by the further simplified version, incorporating (3.7)–(3.10),

$$c_n(\vec{x}_1, \vec{x}_2 | \vec{x}_0; \rho) = [A(\rho, \beta) + \alpha(\rho, \beta)\theta(r_m, R)]\exp\{-[b(\rho, \beta) + \gamma(\rho, \beta)\theta(r_m, R)]r_{12}\}/r_{12}, \tag{3.11}$$

with $\qquad r_{12} = |\vec{x}_1 - \vec{x}_2|, \quad \alpha = (\partial A/\partial\rho)\rho h_0, \quad \gamma = (\partial b/\partial\rho)\rho h_0.$

Equation (3.11) also satisfies (3.4). With (3.11) the integrals on the right-hand side of (3.1) can be reduced to a double quadrature which is susceptible to evaluation by conventional numerical machine computation. We find

$$\beta\Phi(r_{01}) = \ln\left(\frac{A(\rho, \beta)}{r_{01}} e^{-Br_{01}} + 1\right) + \int_0^\rho d\rho' I(r_{01}, \rho, \rho') - 4\pi\int_0^\rho \frac{A(\rho', \beta)}{b^2(\rho', \beta)} d\rho' \tag{3.12}$$

with (case $B^{-1} > 2r_{01}$)

$$\begin{aligned}
I(r_{01}, \rho, \rho') &= \int d\vec{x}_2 [g(\vec{x}_{02}, \rho) c_n(\vec{x}_1, \vec{x}_2 | \vec{x}_0; \rho')] \\
&= 2\pi\int_0^{R - r_{01}} dr \frac{r}{r_{01}} \left(1 + \frac{A(\rho)}{r} e^{-B(\rho)r}\right) \frac{A(\rho') + \alpha(\rho')}{b(\rho') + \gamma(\rho')} \\
&\quad \times (\exp\{-[b(\rho') + \gamma(\rho')]|r_{01} - r|\} - \exp\{-[b(\rho') + \gamma(\rho')](r_{01} + r)\}) \\
&\quad + 2\pi\int_{R - r_{01}}^{R + r_{01}} dr \frac{r}{r_{01}} \left(1 + \frac{A(\rho)}{r} e^{-B(\rho)r}\right) \frac{A(\rho') + \alpha(\rho')}{b(\rho') + \gamma(\rho')} \\
&\quad \times (\exp\{-[b(\rho') + \gamma(\rho')](2r^2 + 2r_{01}^2 - R^2)^{1/2}\} - \exp\{-[b(\rho') + \gamma(\rho')](r + r_{01})\}) \\
&\quad - \frac{A(\rho')}{b(\rho')} \{\exp[-b(\rho')(2r^2 + 2r_{01}^2 - R^2)^{1/2}] - \exp[-b(\rho')(r - r_{01})]\} \\
&\quad + 2\pi\int_{R + r_{01}}^{\infty} dr \frac{r}{r_{01}} \left(1 + \frac{A(\rho)}{r} e^{-B(\rho)r}\right) \frac{2A(\rho')}{b(\rho')} e^{-b(\rho')r} \sinh[b(\rho)r_{01}] .
\end{aligned}$$

Asymptotically for large r_{01} (3.12) reduces to the same result as the PY (2.12) and CHNC (2.13). Unlike the PY or CHNC solutions for $\beta\Phi$ the effective additive pair potential given by (3.12) is not simply scaled by $B(\rho)$ and $b(\rho)$ the ranges of the indirect and direct correlation functions but the effective scales vary with changing ρ. In the absence of an exact analytical or numerically computed $\beta\Phi$ for a three-dimensional system whose h is given by (2.11) it is hard to estimate the relative precision of our three approximate inverse solutions, (3.12), (2.12), and (2.13).

4. EQUATIONS OF STATE

In this Section we turn to the consideration of another inverse problem: Suppose the functional dependence of g on Φ is given, what equations of state are consistent with this assumed form of g? We illustrate this inverse problem by the following example. Suppose the potential of mean force is identified with a scaled pair potential even at nonzero density

$$g(r) = \exp[-\beta\lambda\Phi(r, \rho, \beta)] , \tag{4.1}$$

with λ a dimensionless density-independent scaling factor. Such a g may not be derivable from a many-particle phase-space density. Thus, e.g., the requirement that in the limit as ρ vanishes $g(r) = \exp(-\beta\Phi)$ restricts λ to unity. Still, we can ask what are the equations of state which are consistent with the hypothesis (4.1) with $\lambda = 1$.

To obtain an answer to this question we will eliminate g between the compressibility relation and the virial equation of state. The compressibility relation (2.15) is

$$\partial\rho/\partial X = 1 + 4\pi\rho \int_0^\infty r^2(g-1)\,dr\,, \tag{4.2}$$

while the virial equation of state (2.16) can be rewritten

$$\begin{aligned} X = \rho &+ (2\pi/3)\,\rho^2 \int_0^\infty r^3(\partial/\partial r)(g-1)dr \\ &- 2\pi\rho^3 \int_0^\infty r^2(\partial/\partial\rho)(g-1)\,dr\,. \end{aligned} \tag{4.3}$$

Integrating (4.3) by parts and eliminating $\int_0^\infty r^2 \times (g-1)dr$ from (4.1) gives successively

$$\begin{aligned} X &= \rho - 2\pi\rho^2 \int_0^\infty r^2(g-1)\,dr \\ &\quad - 2\pi\rho^3(\partial/\partial\rho) \int_0^\infty r^2(g-1)\,dr \\ &= \tfrac{3}{2}\rho - \tfrac{1}{2}\rho(\partial/\partial\rho)\rho(\partial\rho/\partial X)\,. \end{aligned} \tag{4.4}$$

Alternatively we can express (4.4) as a second-order nonlinear differential equation for $X = X(\rho)$, $(X' = dX/d\rho)$,

$$\rho X'' + (3 - 2X\rho^{-1})X'^2 - X' = 0\,, \tag{4.5}$$

which is satisfied, in particular, by the ideal gas, $X = \rho$. The origin X, $\rho = 0$ is a singular point of this equation. The transformation $Y = (X')^{-1} + 1 - 2X\rho^{-1}$, $n = (X')^{-1} - 1$ reduces (4.5) to first-order Abel equation, $Y' = dY/dn$,

$$(Y - n)Y'(n) = 2n(1+n)^{-1}\,, \tag{4.6}$$

and does not correspond to a case which can be integrated using a standard, listed, further substitution.

A phase-plane investigation of (4.5) about the origin ρ, $X = 0$ reveals that the only solution of (4.5) which passes through the origin is the ideal gas. Sufficiently near the origin there exists a two-parameter family of solutions of (4.5) whose power-series expansion about $X = 0$ takes the form

$$\rho = \rho_0 + aX + (a/2\rho_0)(3-a)X^2 + (a/6\rho_0{}^2)(7 - 12a + 3a^2)X^3 + \cdots, \quad \rho_0 \neq 0\,, \tag{4.7}$$

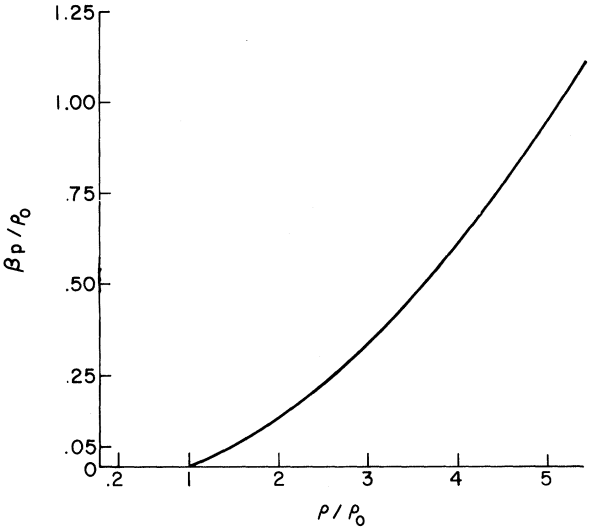

FIG. 1. Equations of state corresponding to solutions of (4.5) for $a = 0.1$.

where X vanishes at $\rho = \rho_0$ and a is the value of the slope $(\partial\rho/\partial X)$ at $\rho = \rho_0$. Figure 1 shows the result of numerical integration of (4.5) (Runge-Kutta method). If $\rho = \rho_0$ is to be a point of mechanical stability, $a > 0$. For $\rho_0 > 0$ the system vanishes at a finite density; while for $\rho_0 < 0$, the system pressure may remain finite at vanishing density. Only very long-ranged (or very singular) potentials will give rise to such equations of state. From (3.1) we note that a necessary condition for (4.1) is that the integral on the right-hand side of (3.1) vanishes identically.

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