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A Contribution to the Equation of State of Fluids at Low Temperatures Based on Thermodynamic Green's Functions

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In quantum statistical mechanics, the Green's function formalism provides an expression for the density of a fluid as a four-dimensional momentum-energy integral over the spectral function. This function can be expressed in terms of the complex self-energy of the single-particle excited states. By using the "ladder diagram" approximation, in a low activity limit at which Fermi–Dirac and Bose–Einstein distributions can be approximated by a Boltzmann distribution, the self-energy has been expressed in terms of the two-body scattering amplitude. Density and pressure can then be expressed in terms of the activity, the temperature, and the two-body scattering phase shifts. A complete numerical evaluation of these results has been made for the case of argon at 100°K, represented by a hard-sphere plus square-well potential: results are presented for the complex self-energy, the density, and the pressure as a function of activity. The resulting equation of state is compared to experimental results represented by the Beattie–Bridgeman equation and good agreement is found for the gaseous part of the 100°K isotherm. Furthermore, two simple analytic equations of state are derived from these expressions with additional (low-density) approximations, which resemble closely some of the equations obtained from the lattice gas theories.

KEY WORDS: Thermodynamic Green's functions; spectral function; self-energy; *T*-matrix; square-well potential; quasiparticles; lattice gas theories.

1. INTRODUCTION

There are several methods available for making theoretical calculations and predictions for the equation of state of fluids, especially the nonconducting fluids.(1,2)

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Thus, one might well ask why one should try and use another method for this purpose. Two areas for improvement (particularly with respect to theories based on the pair distribution function) have been suggested(2,3): (1) the poor predictions given by these calculations at low temperatures (well below the critical temperature T_c), and (2) the intuitive nature of some of the approximations made to obtain the pair distribution function (as, for instance, in the "superposition" approximation.) It is our purpose here to improve on these two points, particularly on the first one.

The theoretical scheme which has been used here for the nonconducting fluids is based on one of the methods suggested by Kadanoff and Baym(4) for obtaining the equation of state from the thermodynamic Green's functions.(5) Basically, it involves expressing the density, through the spectral relations, in terms of the chemical potential μ and temperature T, through the use of the one-particle temperature Green's function. The pressure is then obtained by integrating the thermodynamic identity $dP = n\,d\mu$ (at constant temperature and volume). This was done here for the specific model or approximation of the low-activity, T-matrix approximation,[2] which is proposed for short-range intermolecular potentials and for fluids of molecules obeying Boltzmann statistics. Briefly, the T-matrix approximation includes the effect on the one-particle Green's function or propagator of the n-body collisions made of successive two-body interactions (hence, the name "ladder approximation"). This, unfortunately, stills leads to highly complicated, coupled integral equations for the Green's function and the T-matrix for realistic intermolecular potentials. So, an additional approximation, i.e., of low activity, is made to obtain the self-energy to first order in the activity $z = e^{\mu/kT}$. This, effectively, reduces the self-energy to two-body collisions. The Green's function (and the density) still contains all powers of the activity and the number of collisions, but an error is of course made for higher orders than the second order in z (for the density.) The activity z is known to be small (compared to unity) for all inert gases (except for helium near the λ-point).(6) The low-activity limit also replaces the true statistics by the Boltzmann statistics and thus neglects all symmetry effects. All other quantum effects are, however, retained in our results. The symmetry effects occur only at very low temperatures, thus probably only for helium near the λ-point. The low-activity approximation also replaces the T-matrix by the usual two-body scattering amplitude and the self-energy function becomes the Boltzmann average of the scattering amplitude for zero and π angles.

A complete numerical calculation is then carried out for the density in terms of temperature and activity, for a solvable case, i.e., a hard-sphere plus square-well potential fitted to the second virial coefficient of argon. This potential represents quite well the properties of argon and is much simpler to handle than a Lennard-Jones potential. The pressure is then obtained at $T = 100°\mathrm{K}$, by integrating the relation $dP = n\,d\mu = KTn(z)\,dz/z$. Both parts (real and imaginary) of the self-energy are calculated and used in the density and pressure calculations. The imaginary part is found to have the correct asymptotic behavior and affects the density–pressure calculations quite strongly. The numerical pressure–density results are then compared

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[2] See Kadanoff and Baym,(4) Chapter 13.

to the experimental Beattie–Bridgeman equation of state for gaseous argon at $T = 100°K$. The agreement is excellent for the low-density portion of the curve and the calculated curve shows the proper behavior for the gaseous portion of the isotherm. The disagreement reaches about 9.2% for the highest densities calculated.

2. FORMULATION OF THE PROBLEM

The theory of Green's functions at finite temperature is now well established.(4,7) Let us specify the notations used here. We first define the n-particle Green's function in terms of the field operators for the particles as(4)

$$G_n(1, 2,..., n; 1', 2',..., n') = (-i)^n \langle T_\tau \psi(1)\, \psi(2) \cdots \psi(n)\, \psi^\dagger(n') \cdots \psi^\dagger(1')\rangle \tag{1}$$

where $j = 1, 2,..., n$ stands for $(\mathbf{r}_j, \tau_j)$, $\tau_j = it_j$ is a real variable running from zero to $\beta = (kT)^{-1}$, t_j is the imaginary time, and T_τ is the ordinary τ-ordering operator. If the system is transitionally invariant, the Green's functions can be expanded as usual in Fourier series, for instance,

$$G_1(1 - 1') = (i/\beta) \sum_p \exp\,[-i\omega_p(\tau_1 - \tau_{1'})] \times \int [d^3p/(2\pi)^3] \exp\,[i\mathbf{p}\cdot(\mathbf{r}_1 - \mathbf{r}_{1'})]\, G(\mathbf{p}, \omega_p) \tag{2}$$

with

$$\omega_p = (2p + 1)\,\pi/\beta \quad \text{(FD statistics)}$$
$$= 2p\pi/\beta \quad \text{(BE statistics)}$$

where p is an integer. For a fluid of particles interacting through a two-body potential $v(r)$, the second-quantized Hamiltonian

$$H = \int d^3r\, \psi^\dagger(\mathbf{r})(-\nabla^2/2m)\, \psi(\mathbf{r}) + \tfrac{1}{2} \int d^3r\, d^3r'\, \psi^\dagger(\mathbf{r})\, \psi^\dagger(\mathbf{r}')\, v(|\,\mathbf{r} - \mathbf{r}'\,|)\, \psi(\mathbf{r}')\, \psi(\mathbf{r}) \tag{3}$$

The potential $v(r)$ in Eq. (3) is a typical intermolecular potential, such as the Lennard-Jones potential.

For the ideal gas ($v = 0$), the Fourier transform of the one-particle Green's function in Eq. (2) is

$$G^{(0)}(\mathbf{p}, \omega_p) = [i\omega_p + \mu - (p^2/2m)]^{-1} \tag{4}$$

where μ is the chemical potential. In general, $G(\mathbf{p}, \omega_p)$ is expressed in terms of the irreducible self-energy $\Sigma(\mathbf{p}, i\omega_p)$,(4,7)

$$\begin{aligned} G(\mathbf{p}, \omega_p) &= G^{(0)}(\mathbf{p}, \omega_p)/[1 - \Sigma(\mathbf{p}, i\omega_p)\, G^{(0)}(\mathbf{p}, \omega_p)] \\ &= [i\omega_p + \mu - (p^2/2m) - \Sigma(\mathbf{p}, i\omega_p)]^{-1} \end{aligned} \tag{5}$$

$G(\mathbf{p}, \omega_p)$ can be analytically continued in the upper half-plane of ω, from the points $\omega = i\omega_p$, to yield the retarded Green's function.(7) Similarly, it can be continued in the lower half-plane of ω. The spectral function is defined by(4)

$$\begin{aligned} A(\mathbf{p}, \omega) &= -2\,\mathrm{Im}[G(\mathbf{p}, \omega_p)]_{i\omega_p \to \omega + i\epsilon} \\ &= \frac{-2\,\mathrm{Im}\,\Sigma(\mathbf{p}, \omega + i\epsilon)}{[\omega + \mu - (p^2/2m) - \mathrm{Re}\,\Sigma(\mathbf{p}, \omega + i\epsilon)]^2 + [\mathrm{Im}\,\Sigma(\mathbf{p}, \omega + i\epsilon)]^2} \end{aligned} \tag{6}$$

In the last line of Eq. (6), $i\omega_p$ has been replaced by $(\omega + i\epsilon)$, where ω is a real frequency and ϵ is a real, positive infinitesimal. The equations (1)–(6) have been written for the case in which the Heisenberg representation of the field operators is with respect to $\mathscr{H} = H - \mu N$, where H is the Hamiltonian of Eq. (3) and N is the operator for the total number of particles.

Through the use of the spectral relations,(4,7,8) we obtain immediately an expression for the ensemble average of the number density as a particular value of the corresponding real-time correlation function

$$n = \langle \psi^\dagger(\mathbf{r}, t)\, \psi(\mathbf{r}, t) \rangle = \int \frac{d^3p}{(2\pi)^3} \int \frac{d\omega}{2\pi} \frac{A(\mathbf{p}, \omega)}{e^{\beta\omega} \mp 1} \tag{7}$$

where in this case t is the real time and the upper sign refers to BE statistics and the lower to FD statistics. In a spatially homogeneous system, the average number density n is independent of the position and time variables.[3] Equations (6) and (7) give a relationship connecting the density, chemical potential, and temperature of the system. A differential equation of state(4) relating dn and dP (P is the pressure) at constant temperature can be obtained from these equations and the thermodynamic identity $dP = n\, d\mu$, provided we find, in a suitable approximation, an explicity expression for the self-energy in terms of these parameters.

3. THE EQUATION OF STATE IN THE *T*-APPROXIMATION

The only unknown in Eqs. (6) and (7) is the self-energy function, for which we now choose a realistic approximation, namely the T- or reaction-matrix approximation, as developed for finite temperatures by Kadanoff and Baym(4) (see their Chapter 13). This approximation introduces correlations between the (propagating) particles represented by the two-particle Green's function and is not restricted to a "weak" force. It is thus possible to carry out a calculation for the self-energy in which the strong but short-range interaction between any two particles is taken into account.

We shall further use the limiting case in which the Bose–Einstein and Fermi–Dirac distributions each go over to the Boltzmann distribution: this is obtained formally(4)

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[3] This usual assumption of translational invariance probably excludes the possible coexistence of two phases.

by letting $\beta\mu$ go to $-\infty$ or $e^{\beta\mu}$ go to zero.[(6)] Since $z = e^{\beta\mu}$ is the activity, we shall call this further approximation the low-activity case.

We rewrite Kadanoff and Baym's equations for the self-energy in Fourier space as follows:

$$\begin{aligned}\Sigma(\mathbf{p}, i\omega_p) = \mp\beta^{-1} \sum_{k=-\infty}^{+\infty} \int [d^3p_1/(2\pi)^3]\, G(\mathbf{p}_1, \omega_k) \\ \times [\langle \tfrac{1}{2}(\mathbf{p} - \mathbf{p}_1) \mid T(\mathbf{p} + \mathbf{p}_1, i\omega_p + i\omega_k)\mid \tfrac{1}{2}(\mathbf{p} - \mathbf{p}_1)\rangle \\ \pm \langle \tfrac{1}{2}(\mathbf{p} - \mathbf{p}_1) \mid T(\mathbf{p} + \mathbf{p}_1, i\omega_p + i\omega_k)\mid \tfrac{1}{2}(\mathbf{p}_1 - \mathbf{p})\rangle] \qquad (8)\end{aligned}$$

where the T-matrix represents the sum of all ladder diagrams and is given (in the limit $\beta\mu \to -\infty$) by the following integral equation:

$$\begin{aligned}\langle \mathbf{p} \mid T(\mathbf{P}, i\omega_p)\mid \mathbf{p}'\rangle = v(\mathbf{p} - \mathbf{p}') \\ + \int [d^3\bar{p}/(2\pi)^3]\langle \mathbf{p} \mid T(\mathbf{P}, i\omega_p)\mid \bar{\mathbf{p}}\rangle\, v(\bar{\mathbf{p}} - \mathbf{p}') \\ \times [i\omega_p + 2\mu - (P^2/4m) - (\bar{p}^2/m)]^{-1} \qquad (9)\end{aligned}$$

In Eq. (9), $\omega_p = 2p\pi/\beta$ (p an integer),

$$v(\mathbf{p}) = \int d^3r[\exp(-i\mathbf{p}\cdot\mathbf{r})]\, v(r)$$

and $\mathbf{P}$ is the center-of-mass momentum of the two interacting particles. We recall here[(4,7)] that the T-matrix is the analytic continuation of the usual two-body scattering amplitude where the kinetic energy of relative motion (p^2/m) is replaced by ($i\omega_p + 2\mu - P^2/4m$). Hence, when T is analytically continued from the points $\omega = i\omega_p$, we have the analytic properties[(9)] of T as a function of the complex variable ω: the poles of T occur when ($\omega + 2\mu - P^2/4m$) is equal to the energy E_i of a bound state of the two-particle system and a branch point occurs at $\omega = -2\mu + (P^2/4m) + (\tau^2/4m)$, where $\boldsymbol{\tau} = \mathbf{p} - \mathbf{p}'$.

We now turn to Eq. (8), where the summation over k is performed by contour integration in the complex plane[4] through the use of an auxiliary function which we choose, for BE statistics, to be $2\pi i(e^{i2\pi z} - 1)^{-1}$:

$$\sum_{k=-\infty}^{+\infty} f(k) = -\sum \mathrm{Res}[2\pi i f(z)(e^{i2\pi z} - 1)^{-1}]$$

at the poles of $f(z)$ (Res indicates "residues of"). This relation is valid only if the constraint $\mid zf(z)\mid \to 0$ as $\mid z \mid \to \infty$ is satisfied. This is realized here because of the known properties of the scattering amplitude.[(10)] We shall do the k summation in the limit $\beta\mu \to -\infty$ or to lowest order in $e^{\beta\mu}$: in this limit, we replace G in Eq. (8) by

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[4] See Kadanoff and Baym,[(4)] p. 196.

$G^{(0)}$ defined in Eq. (4), because $\Sigma(\mathbf{p}, i\omega_p)$ is at least$^{(11)}$ of first order in $e^{\beta\mu}$. In this limit, the k summation becomes essentially[5]

$$\begin{aligned}
&\sum_{k=-\infty}^{+\infty} [k(2\pi i/\beta) - (p_1^2/2m) + \mu]^{-1}\, T(i\omega_p + [2\pi i k/\beta]) \\
&\qquad \simeq -\beta T(i\omega_p + [p_1^2/2m] - \mu)\{\exp[\beta(p_1^2/2m) - \mu] - 1\}^{-1} \\
&\qquad \simeq -\beta\{\exp[-\beta(p_1^2/2m) - \mu]\}\, T(i\omega_p + [p_1^2/2m] - \mu) \qquad (10)
\end{aligned}$$

In Eq. (10), we have neglected the residues at the poles of the T-matrix, which are at

$$i\omega_k = E_i - i\omega_p + [(\mathbf{p} + \mathbf{p}_1)^2/4m] - 2\mu.$$

These residues are proportional to $e^{2\beta\mu}$ and are negligible (in the low-activity limit) compared to the terms retained in Eq. (10). Similarly, the contribution from the branch-point singularity is negligible in the same limit. Inserting the expression (10) into Eq. (8), we obtain

$$\begin{aligned}
\Sigma(\mathbf{p}, i\omega_p) = z \int & [d^3p_1/(2\pi)^3][\exp(-\beta p_1^2/2m)] \\
& \times [\langle \tfrac{1}{2}(\mathbf{p} - \mathbf{p}_1) \mid T(\mathbf{p} + \mathbf{p}_1\,, i\omega_p + [p_1^2/2m] - \mu) \mid \tfrac{1}{2}(\mathbf{p} - \mathbf{p}_1)\rangle \\
& \pm \langle \tfrac{1}{2}(\mathbf{p} - \mathbf{p}_1) \mid T(\mathbf{p} + \mathbf{p}_1\,, i\omega_p + [p_1^2/2m] - \mu) \mid \tfrac{1}{2}(\mathbf{p}_1 - \mathbf{p})\rangle] \qquad (11)
\end{aligned}$$

Now, if we substitute Eq. (11) into Eq. (6) and the latter equation into Eq. (7), we obtain an equation of state relating n, μ, and T which involves the T-matrix. Unfortunately, the integral equation (9) for the T-matrix is soluble only for idealized interparticle potentials.$^{(12)}$ However, we can use the limit as $\beta\mu \to -\infty$ to simplify our equations.$^{(11)}$ In this limit, $\Sigma(\mathbf{p}, i\omega_p)$, which is proportional to z, will be small compared to $[(p^2/2m) - \mu]$ in Eq. (5) and $A(\mathbf{p}, \omega)$ of Eq. (6) will be peaked around $\omega \simeq (p^2/2m) - \mu$. So we shall evaluate[6] $\Sigma(\mathbf{p}, \omega + i\epsilon)$ in Eqs. (5) and (6) at the approximate peak of $A(\mathbf{p}, \omega)$ as a function of ω. In Eq. (6),

$$\begin{aligned}
&\Sigma(\mathbf{p}, \omega + i\epsilon) \\
&\quad \simeq \Sigma(\mathbf{p}, [p^2/2m] - \mu + i\epsilon) \\
&\quad = z \int [d^3p_1/(2\pi)^3][\exp(-\beta p_1^2/2m)] \\
&\qquad \times [\langle \tfrac{1}{2}(\mathbf{p} - \mathbf{p}_1) \mid T(\mathbf{p} + \mathbf{p}_1\,, [p^2/2m] + [p_1^2/2m] - 2\mu + i\epsilon) \mid \tfrac{1}{2}(\mathbf{p} - \mathbf{p}_1)\rangle \\
&\qquad \pm \langle \tfrac{1}{2}(\mathbf{p} - \mathbf{p}_1) \mid T(\mathbf{p} + \mathbf{p}_1\,, [p^2/2m] + [p_1^2/2m] - 2\mu + i\epsilon) \mid \tfrac{1}{2}(\mathbf{p}_1 - \mathbf{p})\rangle] \\
&\quad = -(4\pi/m)z \int [d^3p_1/(2\pi)^3][\exp(-\beta p_1^2/2m)] \\
&\qquad \times [f_{(\mathbf{p}-\mathbf{p}_1)/2}(\theta = 0) \pm f_{(\mathbf{p}-\mathbf{p}_1)/2}(\theta = \pi)] \\
&\quad = z\,[S^R(\mathbf{p}) - iS^I(\mathbf{p})] \qquad (12)
\end{aligned}$$

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[5] For FD statistics, this expression has the opposite sign.

[6] If one makes a Taylor expansion of $\Sigma(\mathbf{p}, \omega)$ around $\omega = (p^2/2m) - \mu$, one sees that the terms neglected in Eq. (12) are at least of order z^2.

where $f_{\mathbf{p}}(\theta)$ is the ordinary scattering amplitude for outgoing waves.$^{(13)}$ In Eq. (12), S^{R} and S^{I} are real-valued functions of $\mathbf{p}$ whose definitions are obvious. We note that $S^{\mathrm{I}}(\mathbf{p})$ is positive-valued because it depends on $\operatorname{Im} f_{\mathbf{p}}(0)$, which by the optical theorem is equal to $p\sigma/4\pi > 0$, where σ is the total cross section.

If we combine Eqs. (12), (6), and (7), we obtain easily

$$\begin{aligned} n &= 2\int \frac{d^3p}{(2\pi)^3} \int \frac{d\omega}{2\pi} \frac{zS^{\mathrm{I}}(\mathbf{p})(e^{\beta\omega} \mp 1)^{-1}}{[\omega + \mu - (p^2/2m) - zS^{\mathrm{R}}(\mathbf{p})]^2 + [zS^{\mathrm{I}}(\mathbf{p})]^2} \\ &= 2\int \frac{d^3p}{(2\pi)^3} \int \frac{d\omega}{2\pi} \frac{z^2S^{\mathrm{I}}(\mathbf{p})(e^{\beta\omega} \mp z)^{-1}}{[\omega - (p^2/2m) - zS^{\mathrm{R}}(\mathbf{p})]^2 + [zS^{\mathrm{I}}(\mathbf{p})]^2} \end{aligned} \tag{13}$$

The second expression of Eq. (13) is obtained by the change of variable $\omega + \mu \to \omega$. The expression (13) for the density is, as shown repeatedly in Kadanoff and Baym's treatise,$^{(4)}$ of the general type expected: the total density is equal to the integral over momentum and energy of the product of the spectral function (or probability of occupation of mode ω with momentum $\mathbf{p}$) times the average occupation number of the mode ω. The spectral function is here approximated by a Lorentzian distribution centered around the energy of the quasiparticles, with a width inversely proportional to the lifetime of the quasiparticles. This expression gives us, in principle, n as a function of z and T. To complete the equation-of-state formulation, we need an expression for the pressure P, which is obtained by integrating the thermodynamic identity $n = (\partial P/\partial\mu)_{T,\Omega}$ (Ω is the volume) to yield

$$P = \int_0^{\mu} n\, d\mu' = KT \int_0^z n(z')\, dz'/z' \tag{14}$$

We also need expressions for S^{R} and S^{I}, given by Eq. (12), which are suitable for numerical computations. The most useful ones are in terms of the two-body scattering phase shifts δ_l. Thus, if we write$^{(13)}$

$$f_{\mathbf{p}}(\theta) = (2ip)^{-1} \sum_{l=0}^{\infty} (2l + 1)[\exp(2i\delta_l) - 1]\, P_l(\cos\theta) \tag{15}$$

we obtain

$$\begin{aligned} S^{\mathrm{R}}(\mathbf{p}) &= -\,8/(\pi\beta p)[\exp(-\beta p^2/2m)] \\ &\quad \times \int_0^{\infty} p'\, dp'[\exp(-2\beta p'^2/m)][\sinh(2\beta pp'/m)] \\ &\quad \times \operatorname{Re}[f_{p'}(0) \pm f_{p'}(\pi)] \\ &= -\,(16/\pi\beta p)[\exp(-\beta p^2/2m)] \sum_{l=\text{even or odd}} (2l + 1) \\ &\quad \times \int_0^{\infty} dp'[\exp(-2\beta p'^2/m)][\sinh(2\beta pp'/m)] \\ &\quad \times (\tan\delta_l)/(1 + \tan^2\delta_l). \end{aligned} \tag{16}$$

The summation over l runs, as usual, over even integers for BE statistics and over odd integers for FD statistics. Similarly, one obtains for the imaginary part

$$\begin{aligned} S^{\mathrm{I}}(\mathbf{p}) = {} & 16/(\pi\beta p)[\exp(-\beta p^2/2m)] \sum_{l=\text{even or odd}} (2l+1) \\ & \times \int_0^\infty dp'[\exp(-2\beta p'^2/m)][\sinh(2\beta pp'/m)] \\ & \times (\tan^2\delta_l)/(1+\tan^2\delta_l) \end{aligned} \tag{17}$$

All we need now are results for the scattering phase shifts to calculate S^{R}, S^{I}, n, and P.

4. DISCUSSION OF RESULTS FOR ARGON AT 100°K

We spent a great deal of time trying to obtain analytic solutions of Eqs. (13) and (14) say in terms of the two-body scattering amplitude. Although it is possible to perform some of the integrals (in terms of semiinfinite series), it takes additional approximations to reduce this integral to a more tractable form. In Appendix A, we have used the zero-width approximation for the Lorentzian in Eq. (13) to get simpler results. If one uses in addition a low-density approximation to eliminate the activity between Eqs. (13) and (14), one obtains essentially the analytic equations of state obtained by the simple lattice gas theories, i.e., the noninteracting lattice gas and the quasichemical equation. This is hardly very interesting, but it shows which simplifications to make in the exact Green's function theory to obtain simple results of the lattice gas model. Another analytic problem in Eqs. (13) and (14) is the elimination of the activity between these equations to obtain a closed equation between n and P. The same problem occurs in Mayer's(14) classical theory of condensation and is solved by series expansion, which leads to the virial coefficient series. The virial coefficients of our Eqs. (13) and (14) will be examined similarly in a separate paper. At this point, we turn to "exact" numerical methods of solving Eqs. (13) and (14) without any further approximations.

The set of equations (13), (14), (16), and (17) is all we need to solve the problem of the equation of state in the low-activity T-approximation. The scattering phase shifts δ_l were chosen according to a "square-well" potential (see Fig. 1) fitted to the second virial coefficient data of argon, with the parameters(15) $a = 3.16$ Å, $b = 5.85$ Å, and $\epsilon/k = 69.4$°K. This potential is much easier to handle than a Lennard-Jones potential, for which the phase shifts can only be found by numerical methods. For the square-well potential, one finds, after a simple exercise in quantum mechanics,

$$\tan\delta_l = [pj_l'(pb) - w_l j_l(pb)]/[pn_l'(pb) - w_l n_l(pb)] \tag{18}$$

where

$$w_l = \frac{q[n_l(qa)\, j_l'(qb) - j_l(qa)\, n_l'(qb)]}{n_l(qa)\, j_l(qb) - j_l(qa)\, n_l(qb)}$$

$q = (p^2 + m\epsilon)^{1/2}$, and j_l and n_l are the two types of spherical Bessel function. In Eq. (18), we have continued using $\hbar = 1$, but of course, for numerical calculations,

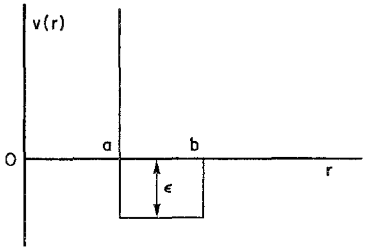

Fig. 1. A "square-well" intermolecular potential.

one has to reintroduce the appropriate powers of $\hbar$, in order to make, say, qa and pb dimensionless quantities.

The real and imaginary parts S^R and S^I of the self-energy (per unit activity) were calculated on a digital computer for the above values of the potential parameters and for temperatures $T = 85°K$ and $100°K$. In this calculation, we used a Chalk River subroutine to generate the spherical Bessel functions in Eq. (18) for all arguments and orders and we used the three-point Simpson's rule to evaluate Eqs. (16) and (17). The test to terminate the integrals was very stringent and the self-energy results are valid to at least four significant figures. The results are presented in Figs. 2 and 3. The real part S^R shows some interesting features: the hard spheres contribute a positive and nearly constant self-energy for a large range of momenta up to $Y = (2/mkT)^{1/2} p \simeq 7$. After this point, S^R becomes negative (effect of attractive forces) and seems to continue oscillating for larger momenta. The addition of zS^R to the kinetic energy $p^2/2m$ gives the spectrum of the quasiparticles in this approximation: this spectrum has oscillations not unlike those found experimentally in

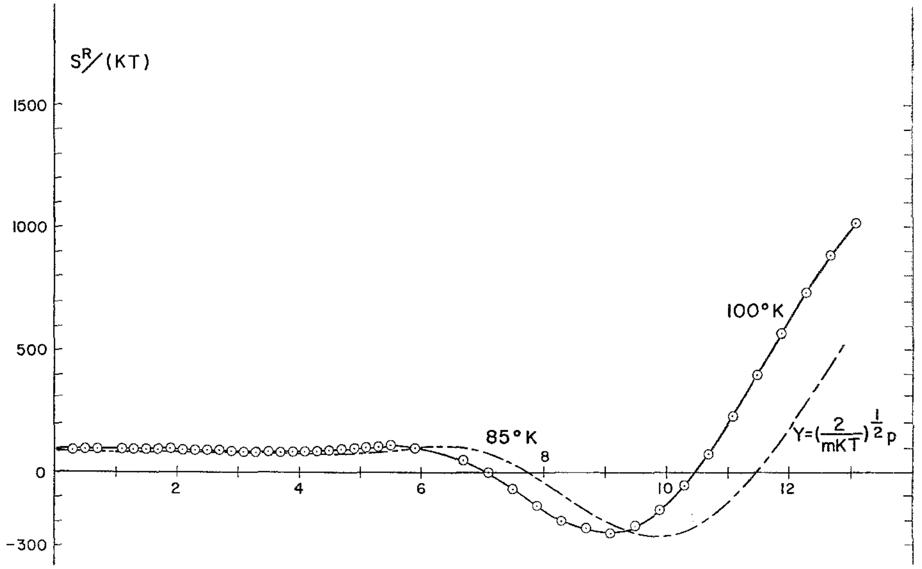

Fig. 2. The real part of the self-energy (per unit activity and thermal energy) vs. a dimensionless momentum for two temperatures: the circles indicate the calculated points for $T = 100°K$.

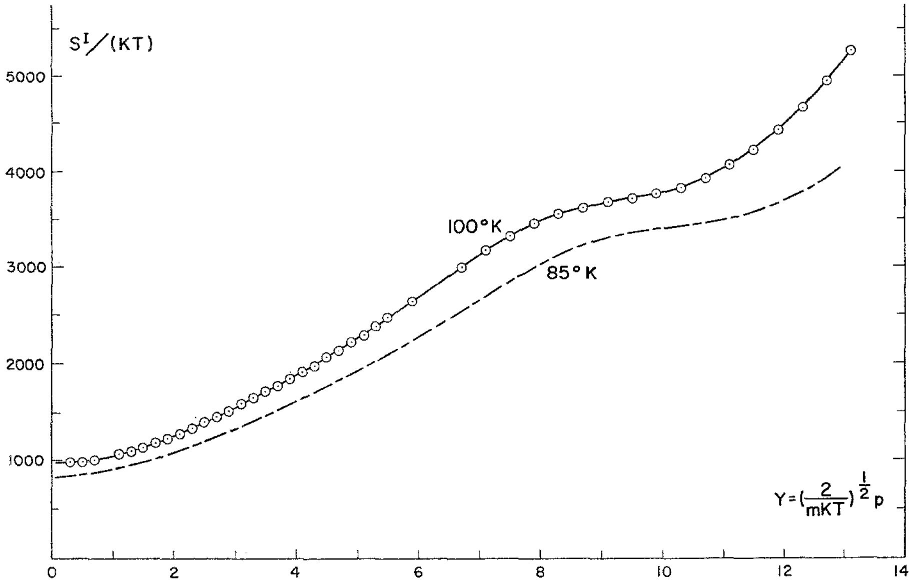

Fig. 3. The imaginary part of the self-energy (per unit activity and thermal energy) vs. a dimensionless momentum for two temperatures.

helium II, but fails to yield the sound-wave part of the spectrum.[7] The first order in the activity for the self-energy seems to exclude the propagation of sound waves. The imaginary part S^{I} behaves much more simply: it quickly reaches its asymptotic form, which is linear in p. Indeed, one can show easily for Eq. (17) that, for large momenta $\mathbf{p}$, the major contribution to the integral comes from large $\mathbf{p}'$, for which $\mathrm{Im} f_{\mathbf{p}'}(0) = p'\sigma/4\pi$, where σ is the constant limiting cross section for hard spheres(13) $(2\pi a^2)$ and this makes $S^{\mathrm{I}}(\mathbf{p})$ linear in $\mathbf{p}$ for large momenta. It is an interesting result that this asymptotic form seems to be good over most of the range with some additional fluctuations. Another result verified numerically was that in Eqs. (16) and (17) one obtains the same result (within numerical errors) in either the BE or the FD case, since we have been using the Boltzmann statistics limit as noted earlier: the pure exchange terms give zero contribution in the Boltzmann case.

We now turn to the evaluation of density and pressure in Eqs. (13) and (14). This is a comparatively easy calculation: the only problem is to find the range of variables contributing to the integrals. For convergence reasons, we could not use the Boltzmann limit of the distributions in Eq. (13), so we used the FD (lower case) distribution to approximate the Boltzmann distribution. We used the following dimensionless form of our integrals for computations:

$$na^3 = \sqrt{2}\,(mkT)^{3/2}(a/h)^3 z^2 \times \int_0^{\infty} Y^2\, dY\, I(Y) \int_{-\infty}^{+\infty} d\Omega \frac{(e^{\Omega} + z)^{-1}}{\{[\Omega - (Y^2/4) - zR]^2 + z^2 I^2\}} \tag{19}$$

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[7] This seems to raise the question of whether these oscillations may be due to the potential and not to BE condensation.

where $Y = (2\beta/m)^{1/2}p$, $\Omega = \omega/kT$, $R(Y) = S^{R}/kT$, $I(Y) = S^{I}/kT$, and a is the hard-sphere diameter. Then,

$$\beta Pa^3 = \int_0^z a^3 n(z')\, dz'/z' \tag{20}$$

The numerical evaluation of Eq. (19) was performed most easily by doing the Ω-integral first and by integrating from the center of the Lorentzian, i.e., $\Omega_p = (Y^2/4) + zR(Y)$, a certain number of half-widths $zI(Y)$ in both directions: we finally settled an integrating over 30 half-widths in each direction with 600 mesh points over the total Ω range. This gave us an accuracy well within 0.5 %. Another check of the accuracy was made by obtaining numerically the correct ideal-gas limit (for $z = 10^{-6}$). The ideal-gas limit ($z \to 0^+$) of Eq. (19) is easily obtained and gives the standard result

$$(na^3)_{\text{ideal}} = (mkT/2\pi)^{3/2}(a/\hbar)^3 z. \tag{21}$$

The Y-integral, being much smoother, was handled with a mesh size $\Delta Y = 0.3$ and up to $Y_{\max} = 10$.

Equation (20) for βPa^3 was also evaluated numerically by Simpson's rule. The initial value (at $z = 0$) of the integrand cannot be evaluated numerically and is taken as given by Eq. (21), which is exact for $z = 0$. All other values of the integrand are, of course, based on the calculated values of na^3 as a function of z.

The results of our calculations at $T = 100$°K are given in Appendix B and in Figs. 4 and 5. The plot of na^3 vs. z in Fig. 4 has the expected shape as compared to

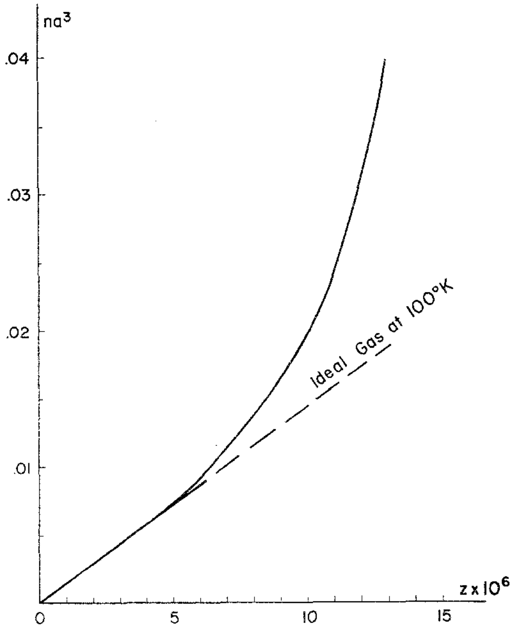

Fig. 4. Density vs. activity in the low-activity T-approximation for argon at 100°K.

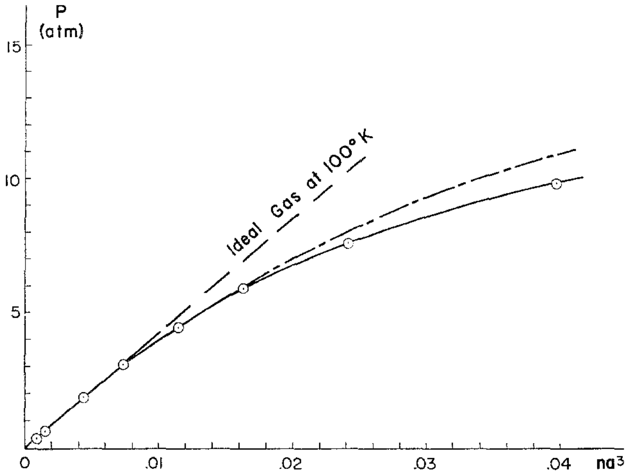

Fig. 5. Pressure vs. density (full curve) in the same model for argon at 100°K: the circles indicate the computer-calculated points. The Beattie–Bridgeman [17] equation of state (dashed curve) has also been plotted for $T = 100°\mathrm{K}$.

similar plots.[16] The plot in Fig. 5 is obtained by eliminating z between na^3 and βPa^3. On the same graph we have plotted the Beattie–Bridgeman equation of state[17] based on the experimental data for argon at $T = 100°\mathrm{K}$: this equation is a semi-empirical, five-parameter equation which represents quite well the experimental data. We could not find any molecular-dynamics or similar computer calculations at 100°K to compare with our calculated results. The comparison is thus more stringent between our calculated results and the Beattie–Bridgeman equation based on the experimental results. One sees that the agreement in Fig. 5 between our calculations and experimental data is quite good for the lowest densities and become less so as the density increases. The general shape of the gaseous equation of state is certainly represented by our theoretical calculations. Our calculations fail, however, to yield the liquid part of the isotherm. Our results seem to go into a phase transition, in the sense that na^3 increases very rapidly as a function of z and the P–n curve tends to go over to a horizontal plateau which corresponds to the coexistence region.

Finally, we discuss at some length how our calculations could be extended to larger z values. First, we note that we are interested, for molecular fluids, in z values less than or equal to unity (for which we have Bose–Einstein condensation for a Bose fluid.) Our calculations could be improved by including contributions to order z^2 in $\Sigma(\mathbf{p}, \omega + i\epsilon)$ used in Eqs. (6) and (7). These contributions would come from three sources: (1) the contributions of the poles and branch-point singularities of the T-matrix to Eq. (10); (2) the contribution of the "off-energy-shell" T-matrices in Eq. (12); (3) the effect of the three-particle terms in the self-energy of Eq. (8), where $G^{(0)}$ is replaced by its first iteration $G^{(1)}$ with a self-energy given by (11).

The first and third of the contributions above are relatively easy to evaluate. The second one is much more difficult since the general T-matrix of Eq. (9) looks difficult to obtain, at least in a closed-form solution. However, a partial-wave expansion should be possible for this general T-matrix. These contributions should, of course, be included in an exact theory of the higher-order virial coefficients.

Thus, in conclusion: (1) our theoretical results in the low-activity T-approximation seem to reproduce quite well the equation of state in the gaseous phase, at $T = 100°\mathrm{K}$; (2) our results fail to yield the liquid part of the isotherm at 100°K: this was to be expected from the low-activity approximation; (3) some simple analytical results are obtained in Appendix A which connect the Green's function theory to the simple lattice gas theories after considerable simplifications; (4) the main drawback in our calculations was the length of computing time involved: we spent nearly 3 hr of IBM 360/65 computing time to obtain the self-energy results, plus over an additional hour of same to obtain the na^3–βPa^3 results.

APPENDIX A. SOME SIMPLE ANALYTIC EQUATIONS IN THE LOW-DENSITY *T*-APPROXIMATION

Equation (13) simplifies considerably if we take the limit as $zS^{\mathrm{I}} \to 0^+$, which we shall call the zero-width limit. (This corresponds to infinite lifetimes for the quasiparticles.) This new approximation is still consistent with the small-activity case, but there seems to be no good reason to neglect S^{I} and not S^{R} in our equations. If we use the relation

$$\lim_{\epsilon\to 0^+} [\epsilon/(x^2 + \epsilon^2)] = \pi\, \delta(x)$$

we obtain easily

$$\begin{aligned} n &= z \int [d^3p/(2\pi)^3] \int d\omega\, \delta[\omega - (p^2/2m) - zS^{\mathrm{R}}(\mathbf{p})](e^{\beta\omega} \mp z)^{-1} \\ &\simeq z \int [d^3p/(2\pi)^3] \exp\{-\beta[(p^2/2m) + zS^{\mathrm{R}}(p)]\} \end{aligned} \tag{A1}$$

Equation (A1) has the expected form for the limiting case of Boltzmann statistics ($z \to 0$). As usual, $zS^{\mathrm{R}}(\mathbf{p})$ can be interpreted as the average energy gained by a particle of momentum $\mathbf{p}$ as the result of its collision with the other particles in the fluid⁽⁴⁾ (in the present approximation). An equation similar to (A1) can be obtained for the pressure. The problem is how to eliminate the parameter z between these equations.

Let us carry out the elimination of z in an approximate manner, i.e., for low densities. This will lead to simple equations of state which resemble closely the results of the lattice gas theories.⁽¹⁸⁾ Following the usual procedure,⁽⁴⁾ let us first differentiate Eq. (A1) at constant β and use $dP = n\, d\mu$:

$$\begin{aligned} dn &= \beta n\, d\mu - \beta^2 e^{2\beta\mu}\, d\mu \\ &\quad \times \int [d^3p/(2\pi)^3] \exp\{-\beta[(p^2/2m) + e^{\beta\mu}S^{\mathrm{R}}(\mathbf{p})]\}\, S^{\mathrm{R}}(\mathbf{p}) \\ &= \beta\, dP\, [1 - (\beta/n)z^2\langle S^{\mathrm{R}} \exp(-\beta S^{\mathrm{R}} z)\rangle] \end{aligned} \tag{A2}$$

where

$$\langle A\rangle = \int [d^3p/(2\pi)^3] A \exp(-\beta p^2/2m)$$

Unfortunately, we need z as a function of n to integrate Eq. (A2) into an equation relating P, n, and T. Let us, for simplicity, express z^2 to order n^3 from Eq. (A1) and let us also put $z = 0$ in the exponential function in (A2): this is a low-density approximation to the square bracket in Eq. (A2). We write

$$z^2 = n^2\langle 1\rangle^{-2} + 2n^3\beta\langle 1\rangle^{-4}\langle S^{\mathrm{R}}\rangle + \mathcal{O}(n^4)$$

and

$$dn = \beta dP[1 - (\beta\langle S^{\mathrm{R}}\rangle/\langle 1\rangle^2)n - (2\beta^2\langle S^{\mathrm{R}}\rangle^2/\langle 1\rangle^4)n^2 + \cdots] \tag{A3}$$

Thus,

$$\begin{aligned} dP &= \frac{kT\,dn}{1 - (n/n_0) - 2(n^2/n_0^2)} \\ &= \frac{2}{3}\frac{kT\,dn}{1 - (2n/n_0)} + \frac{1}{3}\frac{kT\,dn}{1 + (n/n_0)} \end{aligned} \tag{A4}$$

where the parameter

$$n_0 = kT\langle 1\rangle^2/\langle S^{\mathrm{R}}\rangle \tag{A5}$$

Integration of Eq. (A4) with the initial condition $P = 0$ when $n = 0$ yields

$$P = -(n_0kT/3)\log[1 - 2(n/n_0)] + (n_0kT/3)\log[1 + (n/n_0)] \tag{A6}$$

The equation of state (A6), which diverges when $n \to n_0/2$, is very nearly the quasi-chemical equation of state,(16,19) except for the last term: the parameter $n_0/2$ plays the role of a "close-packed" density.

One obtains another result of the lattice gas theory if one uses in (A2) the ideal-gas limit for the square bracket, i.e., from (21),

$$(\beta/n)\, z^2\langle S^{\mathrm{R}}\rangle \simeq (\beta\langle S^{\mathrm{R}}\rangle/\langle 1\rangle^2)\, n = n/n_0 \tag{A7}$$

where n_0 is defined in (A5). Then, the low-density limit of (A2) becomes

$$dn = \beta\, dP[1 - (n/n_0)]$$

or, by integration,

$$P = -n_0kT\log[1 - (n/n_0)] \tag{A8}$$

Equation (A8), which diverges for $n \to n_0$, is exactly the equation of state of the noninteracting lattice gas.(18)

Our results for the low-density T-matrix approximation seem thus to be equivalent to the simple lattice gas theories: this is interesting because it gives a connection between the more physical, although approximate lattice gas model(18) and the more rigorous statistical mechanical theory of thermodynamic Green's functions.

Table I

z	na^3	βPa^3	P_{calc}, atm
2×10^{-7}	0.000287	—	—
6×10^{-7}	0.000861	0.000861	0.371
1×10^{-6}	0.001435	0.001435	0.618
3×10^{-6}	0.004325	0.00431	1.86
5×10^{-6}	0.00730	0.00721	3.11
7×10^{-6}	0.0114	0.01036	4.47
9×10^{-6}	0.0163	0.0138	5.95
1.1×10^{-5}	0.0241	0.0177	7.63
1.3×10^{-5}	0.0397	0.0228	9.85

APPENDIX B. RESULTS FOR CALCULATED EQUATION OF STATE OF ARGON AT 100°K IN THE SQUARE-WELL MODEL

The results shown in Table I have been rounded to three significant figures. The experimental results for P are obtained from the best–fit Beattie–Bridgeman equation.(17)

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