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Equation of state of a classical one-dimensional system with a Lennard-Jones-type potential

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The authors consider a one-dimensional classical system with an interaction potential $v(r) = C_R e^{-\gamma_R r} - C_A e^{-\gamma_A r}$, where C_R, γ_R, C_A, and γ_A are positive parameters. The evaluation of the partition function for this model system is reduced to an eigenvalue problem for a second-order partial differential equation, which is solved by means of the adiabatic approximation. A Van-der-Waals-type equation of state is obtained.

I. INTRODUCTION

With the growing interest in the theory of phase transitions during the last decades there has been an increase in the investigation of model systems which exhibit a first- or second-order phase transition. Among these the one-dimensional systems play a special role: On one hand, the restriction to one dimension yields an enormous simplification of the calculation (the hard-core system, for example, is easily solved in one dimension whereas in three dimensions no exact solution has been constructed so far). On the other hand, fluctuations become exceedingly important in one dimension thereby hindering the formation of an ordered state.[1]

In this work we will study a one-dimensional classical system with a Lennard-Jones–type interaction potential. The potential is written as the sum of a repulsive and an attractive contribution. Both the repulsive and attractive parts of the interaction are of exponential form. This interaction is a modification of the potential used by Kac, Uhlenbeck, and Hemmer[2] (KUH) several years ago: the hard-core part of the interaction used by these authors is replaced by an exponential dependence whereas the attractive part is maintained. Therefore the model potential has the more realistic shape of a Lennard-Jones–type potential (see Fig. 1).

The question will be raised as to whether this type of interaction produces a first-order phase transition. The answer is affirmative in the special limit where the attractive part of the interaction is infinitely weak and slowly decreasing. This result is in agreement with that of KUH who actually introduced this limit in the literature (the so-called Kac-limit). In addition, we approximately calculate the equation of state if the attractive interaction is of finite strength and does not decrease infinitely slowly. Again, in agreement with KUH we find that there is no phase transition in this case but, due to the strong correlation, the equation of state shows some smeared-out discontinuity which is a remnant of a first-order phase transition.

This paper is organized as follows: In Sec. II we formulate the problem of calculating the partition function associated with the exponential interac-

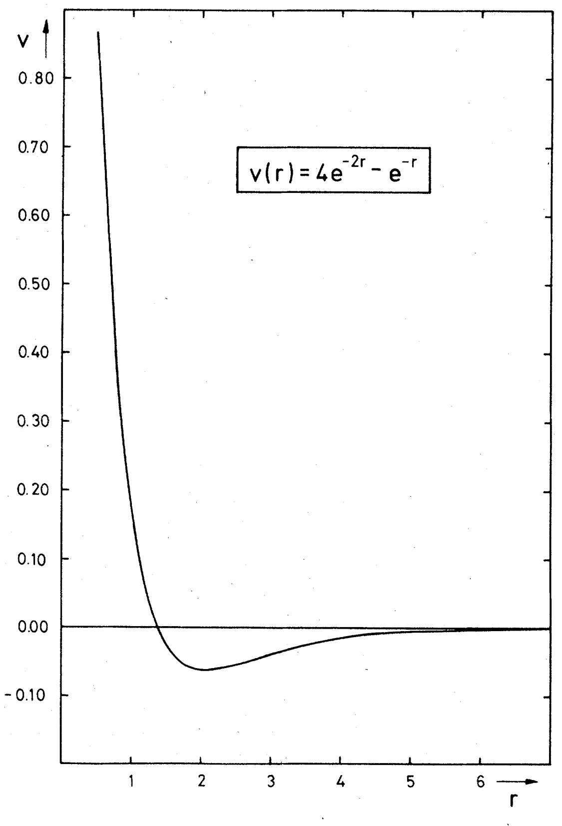

FIG. 1. Interaction potential (2.1) in arbitrary units.

tion potential and recast it in a conventional way to the eigenvalue problem for a second-order partial differential equation with a complex potential. Such an equation, formally similar to those of atomic physics, lends itself to a usual approximation treatment, namely the adiabatic approximation. We discuss thus the application of such techniques in Sec. III. In order to obtain the equation of state we draw upon the results for a "reference" system which has a purely repulsive interaction of exponential form. These results are given in a preceding work,[3] which will be quoted hereafter as I. Finally, in Sec. IV we give the van der Waals limit of the problem and an explicit prescription as to how to implement the Maxwell construction of the isotherms. Known results of KUH are rederived. Some technical points are deferred to the Appendix.

II. FORMULATION OF THE PROBLEM

We will consider a one-dimensional classical system where the particles interact via a two-body interaction given by

$$v(r)=C_R e^{-\gamma_R r}-C_A e^{-\gamma_A r}. \tag{2.1}$$

Here r is the interparticle separation and C_R, γ_R and C_A, γ_A are positive parameters describing the repulsive and attractive parts of the interaction, respectively. The potential (2.1) is shown in Fig. 1 for particular values of the parameters. For a special choice of the parameters it becomes the Morse potential,[4] well-known in molecular physics. In quantum statistical mechanics a potential like (2.1) has been used for the calculation of the structure factor of liquid He^4.[5]

The idea to use a sum of two exponentials as a model potential was inferred from the preceding study I of a purely repulsive potential. There the thermodynamics of a system with the interaction potential

$$v_R(r)=C_R e^{-\gamma_R r} \tag{2.2}$$

has been investigated. The mathematical simplification provided by the exponential dependence of the interaction allows an explicit solution for the equation of state of this system, which is now to be considered as the reference system.

The grand canonical partition function is given by

$$Z_G=1+\sum_{N=1}^{\infty} z^N \int_0^L dx_N \int_0^{x_N} dx_{N-1}\cdots \times\int_0^{x_2} dx_1 \exp\left(-\beta\sum_{i>j=1}^{N} v(|x_i-x_j|)\right),$$

where L is the length of the system and z is the activity of a system of particles of mass m at chemical potential μ:

$$z=(2m\pi/\beta h^2)^{1/2}e^{\beta\mu}.$$

β denotes the inverse temperature T: $\beta=(k_BT)^{-1}$, k_B is Boltzmann's constant and h is Planck's constant.

Invoking the same method developed in I, one may show that the evaluation of the grand canonical partition function for the potential (2.1) is reduced to the calculation of the ground-state eigenvalue of the Hamiltonian operator

$$\mathcal{H}=\gamma_R c^\dagger c+\gamma_A d^\dagger d-z e^{i\lambda_R c^+}e^{i\lambda_R c}e^{\lambda_A d^+}e^{\lambda_A d}, \tag{2.3}$$

where c, c^+ and d, d^+ are two pairs of independent Bose operators, i.e.,

$$[c,c]=[c^+,c^+]=0,\quad [c,c^+]=1$$

(and the analogous relations for d, d^+), whereas the commutators involving c and d operators vanish. The parameters λ_R and λ_A are related to the temperature by

$$\lambda_i=(\beta C_i)^{1/2},\quad i=R,A.$$

The pressure p is given through the ground-state eigenvalue $\epsilon_0(z)$ by the relation

$$\beta p=-\epsilon_0(z), \tag{2.4a}$$

whereas the particle number density ρ is obtained from

$$\rho=-z\frac{d}{dz}\epsilon_0(z). \tag{2.4b}$$

Since $\mathcal{H}$ is a non-Hermitian operator, some care has to be taken in what we mean by ground-state energy $\epsilon_0(z)$: The eigenvalues of $\mathcal{H}$ will occur in complex conjugate pairs[3] which may be ordered with respect to their real part. $\epsilon_0(z)$ then denotes the eigenvalue with the smallest real part which, according to the thermodynamic relations (2.4a), and (2.4b) should have zero imaginary part.

In the space of square integrable functions of two real variables x and y, a canonical representation for the operators c, c^+ and d, d^+ is given by

$$c=\frac{1}{\sqrt{2}}\left(x+\frac{\partial}{\partial x}\right),\quad c^+=\frac{1}{\sqrt{2}}\left(x-\frac{\partial}{\partial x}\right),$$

and an analogous relation for d and d^+. In this space the Hamiltonian operator (2.3) is represented by

$$\mathcal{H}=\tfrac{1}{2}\gamma_R\left(-\frac{\partial}{\partial x^2}+x^2-1\right)+\tfrac{1}{2}\gamma_A\left(-\frac{\partial^2}{\partial y^2}+y^2-1\right) -\zeta e^{i\kappa_R x}e^{\kappa_A y}, \tag{2.5}$$

where

$$\zeta=z e^{\beta C_R/2}e^{-\beta C_A/2}$$

is a renormalized activity and

$$\kappa_i = (2\beta C_i)^{1/2}, \quad i = R,\ A.$$

The eigenvalue problem is then written as

$$\mathcal{H}\psi(x,y) = \epsilon(z)\psi(x,y).$$

III. ADIABATIC APPROXIMATION

We are interested in the ground-state eigenvalue problem of the Hamiltonian (2.5) which includes a complex potential. In order to find the ground-state energy $\epsilon_0(z)$ at least approximately, we use the fact that for realistic applications the parameter γ_R is very large compared to γ_A, i.e., $\gamma_R \gg \gamma_A$, that is, the repulsive part of the interaction decreases over a very short length γ_R^{-1}, whereas the attractive part of the interaction has a very long range γ_A^{-1}. We then see from Eq. (2.5) that the kinetic energy term $\frac{1}{2}\gamma_A\ \partial^2/\partial y^2$ associated with γ_A is much smaller than that associated with γ_R. If we further identify the parameters γ_R and γ_A with inverse masses, we may interpret Eq. (2.5) as the Hamiltonian for a system consisting of a light particle with mass γ_R^{-1} (the "electron" in the language of atomic physics) and a heavy particle with γ_A^{-1} (the "nucleus"). Both particles are coupled via the interaction energy

$$-\zeta e^{i\kappa_R x} e^{\kappa_A y}.$$

It therefore seems reasonable to apply the adiabatic approximation to (2.5) and, in the first step, to neglect the second derivative in y altogether, thus studying the modified eigenvalue problem:

$$\left[\tfrac{1}{2}\gamma_R\left(-\frac{\partial^2}{\partial x^2}+x^2-1\right)-\zeta_{\mathrm{eff}}(y)e^{i\kappa_R x}\right]f(x,y) = E(y,z)f(x,y), \qquad (3.1)$$

where y is considered as a parameter (the "nucleus" coordinate) and

$$\zeta_{\mathrm{eff}}(y) = z e^{\beta C_R/2} e^{-\beta C_A/2} e^{\kappa_A y}.$$

The "energies" E and ϵ are related by

$$E(y,z) = \epsilon(y,z) - \tfrac{1}{2}\gamma_A (y^2-1). \qquad (3.2)$$

$\epsilon(y,z)$ will then play the role of the potential energy in the eigenvalue problem for the "nucleus":

$$\left(-\tfrac{1}{2}\gamma_A \frac{\partial^2}{\partial y^2} + \epsilon(y,z)\right)g(y) = \epsilon(z)g(y). \qquad (3.3)$$

A sufficient condition for the applicability of the adiabatic approximation is[6]

$$\omega \ll |\epsilon_1 - \epsilon_0|,$$

where $\omega \propto \sqrt{\gamma_A}$ is the frequency of the "nucleus" vibrations within the harmonic approximation, that is, when one expands the potential energy $\epsilon(y,z)$ up to second-order terms in y. ϵ_1 and ϵ_0 are the minima of the first excited state $\epsilon_1(y,z)$ and ground state $\epsilon_0(y,z)$, respectively. As long as $\epsilon_1 \neq \epsilon_0$, this condition may always be satisfied by choosing γ_A small enough. An argument that $\epsilon_1 \neq \epsilon_0$ will always be realized is given below.

Essentially the same eigenvalue equation as (3.1) has been studied in I in a calculation of the thermodynamics of a purely repulsive system with the interaction (2.2). There we encountered the following eigenvalue problem[7]:

$$\left[\tfrac{1}{2}\gamma_R\left(-\frac{\partial^2}{\partial x^2}+x^2-1\right)-z e^{\beta C_R/2} e^{i\kappa_R x}\right]\psi(x) = E(z)\psi(x). \qquad (3.4)$$

Hence the knowledge of the solution of this eigenvalue problem provides a basis for the calculation of $E(y,z)$ and by means of (3.2) and (3.3) one may find $\epsilon(z)$.

The adiabatic approximation fits into the general scheme proposed by Lebowitz and Penrose[8] and others.[9] These authors suggest the following procedure: Given a two-body interaction potential written as a sum of a purely repulsive and a purely attractive contribution. In a first step, calculate the thermodynamics for a system where the attractive part of the interaction is turned off (the reference system). In a second step, include the effect of the attractive interaction as a perturbation. This two-step procedure is analogous to the application of the adiabatic approximation, where one first has to know the eigenvalue of the reference system [Eq. (3.4)], and then includes the attractive interaction through Eqs. (3.1) and (3.3).

It therefore turns out that the adiabatic approximation provides us with a useful guideline when we decouple the treatment of the comparatively short-range repulsive part of the potential (described by γ_R and C_R) from the weak attractive part of the interaction (parameters γ_A and C_A). This scheme of decoupling seems to work even when γ_R is not very much larger than γ_A (say $\gamma_R/\gamma_A = 2$, as will be used for the numerics in later sections).

As from general arguments[10] it is known that the reference system shows no phase transition, we may conclude that a level crossing ($\epsilon_1 = \epsilon_0$) will not occur.

IV. DERIVATION OF THE EQUATION OF STATE

In order to obtain the equation of state we have to find the ground-state eigenvalue of Eq. (3.3). The effective potential $\epsilon(y,z)$ in which the "nucleus" moves is determined from $E(y,z)$ by Eq. (3.2). (From now on both ϵ and E refer to the ground state only.) The function $E(y,z)$ is obtained from the ground-state eigenvalue $E(z)$ of the purely repulsive system by the substitution

$$z \to z e^{-\beta C_A/2} e^{\kappa_A y}, \tag{4.1}$$

that is,

$$E(y,z) = E(z e^{-\beta C_A/2} e^{\kappa_A y}) \tag{4.2}$$

[see Eq. (3.1) and Eq. (3.4)]. $E(z)$ is known from I. The main equations for the determination of $E(z)$ are summarized in the Appendix. $E(z)$ is a monotonically decreasing function of z. Hence, as a consequence of (4.2), $E(y,z)$ is a monotonically decreasing function of y. For $z/\gamma_R = 1$ the potential $\epsilon(y,z)$ is shown in Fig. 2. (From now on, the parameter values for the interaction potential are those of Fig. 1.) $\epsilon(y,z)$ is an asymmetric double-well potential implying a first-order phase transition. For higher temperatures the double well disappears and there remains only a single minimum.

A first estimate of the ground-state energy $\epsilon(z)$ can be obtained by the mean-field approximation where we take the minimum of the potential $\epsilon(y,z)$ as the approximate eigenvalue of (3.3), thereby neglecting fluctuations. The extremum condition is

$$\frac{\partial \epsilon(y,z)}{\partial y} = 0, \tag{4.3}$$

which determines the abscissa $y^* = y^*(z)$ of the extremum value. The ground-state eigenvalue $\epsilon_0(z)$ in the mean-field approximation is then given by $\epsilon_0(z) \simeq \epsilon^*(z)$, where

$$\epsilon^*(z) \equiv \epsilon(y^*, z) = E(y^*, z) + \tfrac{1}{2}\gamma_A (y^{*2} - 1). \tag{4.4}$$

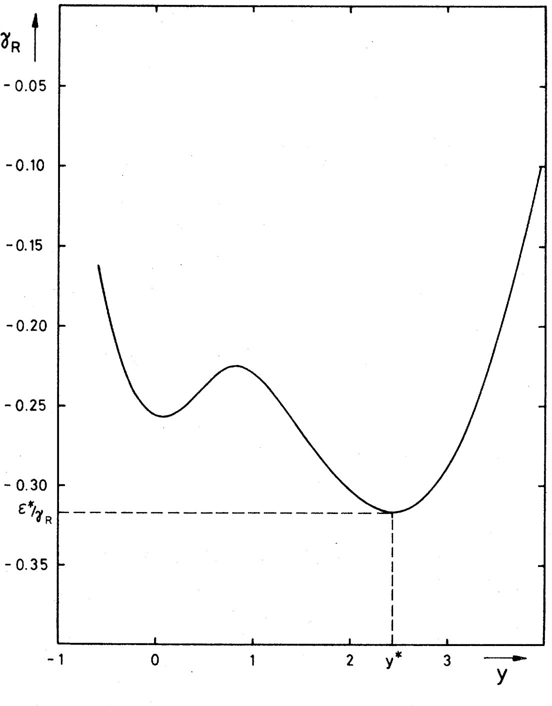

FIG. 2. Effective potential $\epsilon(y,z)$ for $z/\gamma_R = 1$ and $\beta C_R = 40$.

The extremum condition (4.3) may then be written as

$$-\gamma_A y^* = \frac{\partial E(y^*, z)}{\partial y^*}. \tag{4.5}$$

For the determination of the density ρ we have to calculate

$$\rho = -z \frac{d\epsilon^*(z)}{dz} = -z\left(\frac{\partial E(y^*, z)}{\partial z} + \frac{\partial E(y^*, z)}{\partial y^*}\frac{dy^*}{dz} + \gamma_A y^* \frac{dy^*}{dz}\right).$$

The last two terms add up to zero because of the extremum condition (4.5), hence

$$\rho = -z \frac{\partial E(y^*, z)}{\partial z}. \tag{4.6}$$

Eq. (4.6) determines the density ρ as a function of z.

We now want to express the right-hand side of Eq. (4.4) as a function of ρ rather than as a function of z. In order to do this we have to express $E(y^*, z)$ and $y^*(z)$ as functions of ρ. As is shown in the Appendix,

$$E^* = -\beta p'_{\mathrm{ref}}(\rho), \tag{4.7}$$

where $E^* \equiv E(y^*, z)$ and $p_{\mathrm{ref}}(\rho)$ is the pressure of the reference system expressed as a function of ρ. Furthermore, we see from (4.2) that

$$\frac{\partial}{\partial y}E(y,z) = \kappa_A z \frac{\partial}{\partial z}E(y,z). \tag{4.8}$$

By means of Eqs. (4.5) and (4.6), we then obtain from Eq. (4.8)

$$y^* = (\kappa_A/\gamma_A)\rho \tag{4.9}$$

(Note that y^* is up to a constant factor identical to the equilibrium density ρ, which shows that y may be interpreted as a density variable).

Recalling that $\epsilon^*(z) = -\beta p$ the equation of state (4.4) may be written as

$$\beta p = \beta p_{\mathrm{ref}}(\rho) - \tfrac{1}{2}(\kappa_A^2/\gamma_A)\rho^2 + \tfrac{1}{2}\gamma_A, \tag{4.10}$$

where Eqs. (4.7) and (4.9) have been used. Equation (4.10) is essentially the equation of state as found by Lebowitz and Penrose[8]: These authors considered the interaction potential in the so-called Kac-limit where the attractive part of the interaction becomes extremely weak and long ranged, that is, one sets $C_A = \alpha\gamma_A$ and considers the limit

$\gamma_A \to 0$. In this limit Eq. (4.10) becomes

$$\beta p = \beta p_{\mathrm{ref}}(\rho) - \beta \alpha \rho^2 , \tag{4.11}$$

which is identical to the result of Lebowitz and Penrose.

Lebowitz and Penrose do not specify in detail the repulsive part of the interaction which determines $p_{\mathrm{ref}}(\rho)$. They only restrict the reference potential to contain a hard core and to be of finite range. They conjecture that this result will remain valid when less stringent restrictions are put on the repulsive part of the potential. Eq. (4.11) justifies their conjecture as the reference system considered here neither contains a hard core, nor is it of finite range.

The Maxwell construction is contained in (4.10): If $\epsilon(y, z)$ happens to have two minima we take the absolute minimum at y^*, thereby constructing a unique function $\epsilon^*(z) \equiv \epsilon(y^*, z)$. If the two minima become equal there will be a sudden change in the slope of $\epsilon^*(z)$ giving rise to a first-order phase transition within the mean-field approximation.

A. Example: the van der Waals limit

The van der Waals equation of state may be obtained very easily from (4.11). To this end we let the repulsive interaction $v_R(r)$ decrease over a very short range, γ_R^{-1}, and become infinitely steep at some hard-core radius b, that is, we put

$$v_R(r) = C_0 e^{-\gamma_R (r-b)}$$

and consider $\gamma_R \to \infty$. In this limit the repulsive part of the interaction becomes a hard-core interaction. As we showed in I, the pressure of the reference system is then given by the hard-core equation of state

$$\beta p_{\mathrm{ref}}(\rho) = \rho/(1 - b\rho) \quad \text{(hard core)}.$$

Used in (4.11) this directly leads to the van der Waals equation of state.

This result has been obtained by several authors.[2,11,12] Here it serves as a check that the approximations used preserve the basic physical features.

The van der Waals equation of state gives the critical point values. The potential $\epsilon(y, z)$ may then be expanded in powers of y at the critical point.[13] One thereby obtains a Landau expansion for the liquid-gas transition. As noted before, the variable y is related to the density. Odd powers in the density occur as is typical for a first-order phase transition. By also taking the derivative term in Eq. (3.3) into account, the appropriate Ginzburg-Landau expansion is obtained, yielding a relation between γ_A and the Ginzburg-Landau correlation length (see Ref. 13 for the details).

B. Construction of the isotherms

We now want to calculate the isotherms where neither the repulsive interaction is replaced by a hard core, nor the Kac-limit taken for the attractive interaction. Equation (4.10) is the equation of state for our model system with the interaction potential (2.1). The pressure $p_{\mathrm{ref}}(\rho)$ for the reference system with the purely repulsive interaction has been calculated in I.

In Fig. 3 the pressure-versus-density curves are plotted for several values of the temperature. The isotherms all go to a finite value $\frac{1}{2}\gamma_A$ for $\rho \to 0$. This is an unphysical feature that results from the exclusion of the kinetic energy term $-\frac{1}{2}\gamma_A \partial^2/\partial y^2$ in Eq. (2.5), thereby retaining the constant energy shift $-\frac{1}{2}\gamma_A$ in the potential $\epsilon(y, z)$. The authors have reason to believe that this constant shift will disappear in an exact treatment of Eq. (3.3), i.e., if one goes beyond the mean-field approximation.

For low temperatures and small densities the quadratic dependence in ρ dominates in Eq. (4.10) such that the isotherms bend down and a van der

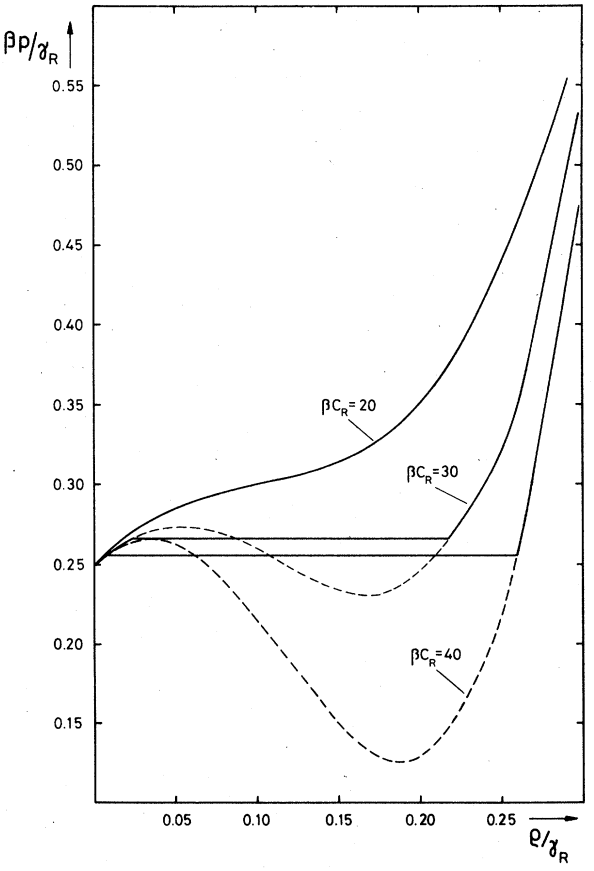

FIG. 3. Isotherms constructed from Eq. (4.10).

Waals-type equation of state is obtained. Therefore the Maxwell construction has to be carried out explicitly. The technical points are explained in the Appendix. Figure 4 shows βp-vs-z curves which are constructed by elimination of the parameter E^* among Eqs. (A5) and (A6) in the appendix. For very low temperatures the curves have three branches: For some values of z there are three values of βp corresponding to the three extremum values of $\epsilon(y, z)$ (see Fig. 2). However, we must obtain βp as a single valued function of z by choosing the branch of βp which corresponds to the absolute minimum of $\epsilon(y, z)$ (solid line in Fig. 4). Then βp shows a jump in slope corresponding to a liquid-gas transition. The pressure at which this jump occurs is used to determine the horizontal segments of the isotherms in Fig. 3 (Maxwell construction).

Thus, within the mean-field approximation, we find a van der Waals type equation of state including the classical Maxwell construction as known from the textbooks of thermodynamics.[14] Of course, for finite γ_A, upon inclusion of quantum fluctuations [i.e., by treating the eigenvalue problem (3.3) quantum mechanically] the first-order phase transition will be smeared out giving rise to an analytic dependence of the pressure as a function of z. Only in the Kac-limit ($\gamma_A \rightarrow 0$) does the discontinuity persist and we have a first-order phase transition in agreement with the results of

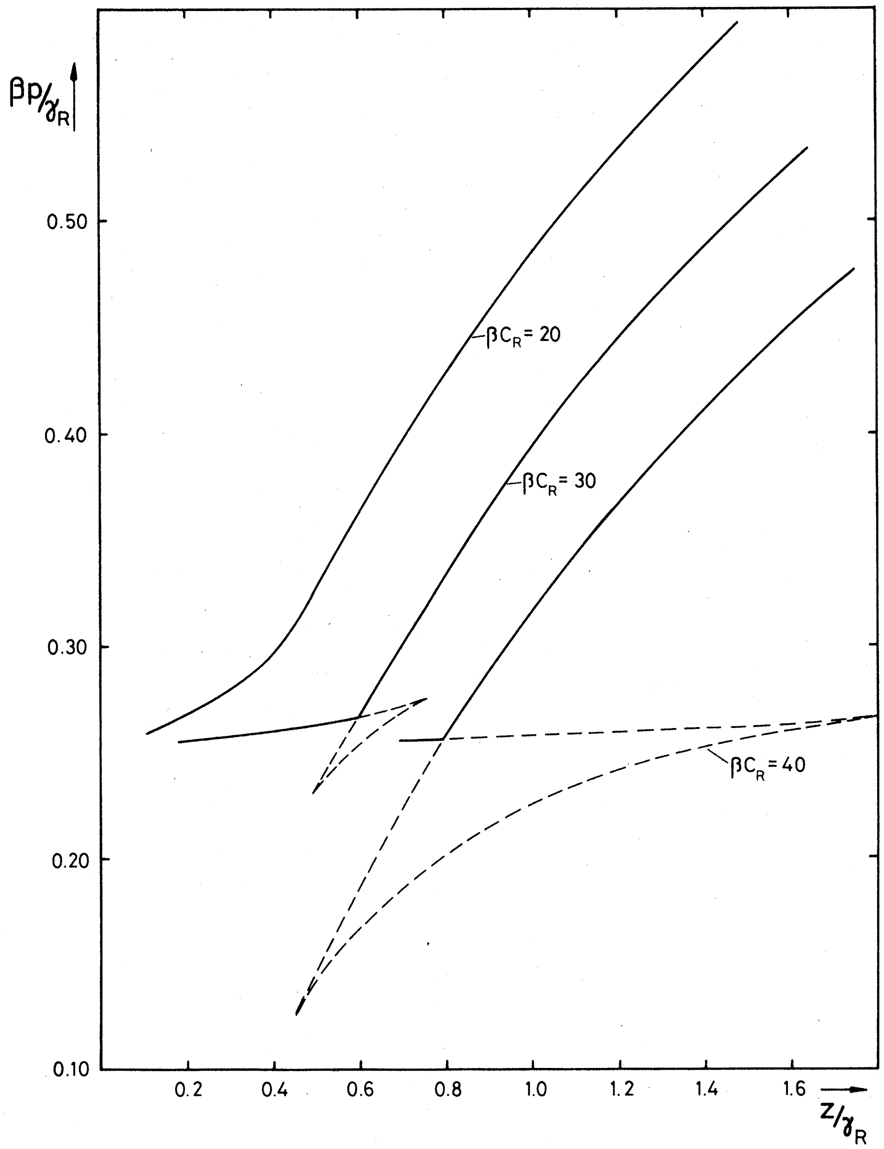

FIG. 4. Pressure p as a function of the activity z for different temperatures.

previous authors.[2,8]

Although the repulsive part of the potential used in this work may be considered as a "soft core", we were not able to find a second phase transition, i.e., a second bending-down of the pressure-versus-density isotherms in Fig. 3. Thus we have found a counterexample to the conjecture of Stell and Hemmer[15] who argue that a softening of the hard core will produce a *second* phase transition (in addition to the one transition already present). The second phase transition found by these authors for a "shouldered" hard-core interaction has to be considered as a particular feature of the form of the potential they used. It should be regarded as a dimerization.[16]

VI. SUMMARY

In this work we have extended a previous study of a one-dimensional classical system. Besides the repulsive interaction investigated before, we have included an exponential attractive interaction thereby forming a two-body interaction potential of the Lennard-Jones–type.

The evaluation of the grand canonical partition function is reduced to a non-Hermitian partial differential equation. This eigenvalue equation is solved by means of the adiabatic approximation.

The system exhibits a first-order phase transition if the attractive part of the interaction is infinitely weak and slowly decreasing (Kac-limit). There is no sharp phase transition if the Kac-limit is not taken but some remnant of the transition is seen in the equation of state.

APPENDIX

In the low-temperature regime the function $E(z)$ is determined as solution of the implicit equation

$$(z/\gamma_R)^{-1} = I(-E/\gamma_R), \tag{A1}$$

where $I(a)$ is defined as the integral[17]

$$I(a) = \int_0^\infty \frac{dt}{t} e^{-\beta C_R t} t^a (1+t)^a .$$

As $E(z)$ has a unique inverse $z(E)$ one may define a function $R(E)$ by

$$R(E) = -z\frac{dE(z)}{dz}, \tag{A2}$$

which is just the density of the reference system as a function of E. The equation of state of the reference system is given by

$$\rho = R(-\beta p_{\text{ref}}) \tag{A3}$$

as an implicit relation for the pressure $p_{\text{ref}}(\rho)$.

Using the definition (A2) together with the relation (4.2) one may write Eq. (4.6) in the text as follows:

$$\rho = R(E^*), \tag{A4}$$

where

$$E^* \equiv E(ze^{-\beta C_A/2}e^{\kappa_A y^*}) = E(y^*, z).$$

This is precisely the same functional dependence as for the equation of state of the reference system (A3). Hence, we may identify

$$E^* = -\beta p_{\text{ref}}(\rho).$$

In order to carry out the Maxwell construction we insert the substitution (4.1) into (A1), set $y = y^*$, and express y^* through $R(E^*)$ by means of (4.9) and (A4). Thus one has

$$\frac{z}{\gamma_R} = \exp\left[\frac{\beta C_A}{2} - \frac{\kappa_A^2}{\gamma_A}R(E^*) - \ln I\left(\frac{-E^*}{\gamma_R}\right)\right]. \tag{A5}$$

By setting $\epsilon^*(z) = -\beta p$ in Eq. (4.4) one further obtains

$$\beta p = -E^* - \tfrac{1}{2}(\kappa_A^2/\gamma_A)[R(E^*)]^2 + \tfrac{1}{2}\gamma_A, \tag{A6}$$

where again, as in (A5), y^* was eliminated in favor of $R(E^*)$. Eqs. (A5) and (A6) give a parametric representation of the pressure as a function of the activity z, E^* being the parameter.

From (A1) we find by implicit differentiation

$$R(E) = -\gamma_R \frac{I(-E/\gamma_R)}{I'(-E/\gamma_R)},$$

where the prime denotes a derivative with respect to the argument. This gives an explicit expression of the function $R(E)$.

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