Transfer matrix approach to the multicomponent Takahashi gas

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Abstract. The exact equation of state for the continuum gas of k components in one dimension has been derived with the help of the transfer matrix method. The gas is represented by rods having the same size and finite range of interaction not exceeding their size. The discussion of the properties of the system subject to constant pressure has been made in the case when the gas consists of two components A and B.

1. Introduction

The multicomponent interacting gas of particles can serve as a model for many physical applications. In particular, in two space dimensions the analysis of the equation of state in the Bragg approximation [1] for the binary alloy indicates the coexistence of the two separate phases of particles, say, of the sort A and B, or one mixed phase depending on the interaction between the particles. How complex the phase portrait is can be determined, e.g. from the examination of adsorption phenomena [2] on a metal surface. In most biological applications it is important to keep the pressure constant. Then, depending on the sign of the interaction between the particles the change in pressure can influence the phase transition from the open structure to the closed one [2, 3]. This type of model nicely describes the anomalous water properties in low temperatures, i.e. the growth of the particle density (or diminishing of the specific volume per particle) with increasing temperature.

In the following we describe the equilibrium properties of the continuum k-component gas of rods in one space dimension. We should mention that the theory of the one-dimensional two-component gas has been considered by Kikuchi [4] and his method has been extended to the case of multicomponent mixtures by Longuet-Higgins [5]. However our approach seems to be simpler. In the model each of the gas components is the short-range interacting Takahashi gas [6]. We analyse its ground state properties and this should reveal the complexity which one can expect in higher dimensions.

2. Formulation of the model

The construction of the model consists of two steps. We start from the lattice gas approximation and then the continuum limit (lattice constant goes to zero) is performed on the lattice gas equation of state. Unless we specify the particular case of the two

sorts of particles our considerations will hold for the general σ-component ($\sigma = 1, \ldots, k$) gas. The particles in the model are represented by rods having the same length s. We assume the two-particle short-range interaction for the gas. The range of each interaction does not exceed the distance s (the rod size).

In the derivation of the continuum equation of state for the system of rods we follow the approach of Shulepov and Aksenenko [2], which is based on the transfer matrix method, and we generalize it to the case of the interacting rods.

Suppose that we have a linear lattice with L sites and we put on it N_σ rods of the sort σ ($\sigma = 1, \ldots, k$). If d is the number of the lattice sites covered by a rod and d_0 is the rod length per one site ($s = dd_0$) then each rod can be divided into d equally spaced segments. These segments we can label with numbers from 1 to d remembering that in one dimension the ordering is always possible. One should notice that, in a similar way, it is possible to label the empty lattice sites between the rods at the distance in the range of their mutual interaction. Thus each lattice site can appear in the following states: it can be covered by one of the d segments of a σ-rod, it can be located in the range of the interaction between the rods or the site is far from the interaction range for the rods. In the model, the rods do not interact if the number of the sites between their closest ends is equal or greater than d. Hence, only the states

$$i^\sigma = (1^\sigma, 2^\sigma, \ldots, 2d^\sigma) \tag{2.1}$$

where $\sigma = 1, \ldots, k$, are sufficient to calculate the partition function of the system of rods. The labels $1, 2, \ldots, 2d$ measure the number of the lattice sites starting from the left end of the σ-particle. We add all contributions to the partition function with the help of the transfer matrix, M, defined as usually for the nearest-neighbour lattice site states (i_r^σ, j_{r+1}^ν), where $r = 1, \ldots, L$ labels the lattice sites and their states are given by (2.1). All non-zero elements of the matrix M are defined as follows

$$M^{\sigma\sigma}(i, i+1) = 1 \tag{2.2a}$$

$$M^{\sigma\sigma}(2d, 2d) = 1 \tag{2.2b}$$

$$M^{\sigma\nu}(i, 1) = z_\nu w_{\sigma\nu}(i+1-d) \qquad \text{for } d \leqslant i < 2d \tag{2.2c}$$

$$M^{\sigma\nu}(2d, 1) = z_\nu \tag{2.2d}$$

where z_σ is the chemical activity ($z_\sigma = e^{\beta\mu_\sigma}$) for rod of the sort σ, and

$$w_{\sigma\nu}(i+1-d) = \exp(\beta J_{\sigma\nu}(i+1-d)) \tag{2.3}$$

is the Boltzmann weight factor for the interaction $J_{\sigma\nu}$ between the rods separated by the distance of $i+1-d$ lattice sites. In general, the interaction potential $J_{\sigma\nu}$ depends on the separation distance between the particles.

In the case of the periodic boundary conditions the partition function reads as

$$Q_L = 1 - k + \text{Tr } M^L \tag{2.4}$$

where k is the number of the gas components and the term $1 - k$ is necessary to subtract the contribution to the sum over configurations when there are no particles. It appears that the eigenvectors of the matrix M have simple structure, which allows us to retrieve the equation of state for the system of rods although it is not possible to find its eigenvalues in the general case. The transfer matrix M satisfies the equation

$$MV = \lambda V \tag{2.5}$$

where $V = [V^1, V^2, \ldots, V^k]^T$ denotes the eigenvector belonging to the eigenvalue λ, and V^σ with $\sigma = 1, \ldots, k$ are the block-vectors consisting of d components. The matrix equation (2.5) can be written explicitly as the following set of equations

$$V^\sigma(i+1) = \lambda V^\sigma(i) \qquad \text{for } 1 \leq i < d \tag{2.6a}$$

$$\sum_{\nu=1}^k z_\nu w_{\sigma\nu}(i+1-d) V^\nu(1) + V^\sigma(i+1) = \lambda V^\sigma(i) \qquad \text{for } d \leq i < 2d \tag{2.6b}$$

$$\sum_{\nu=1}^k z_\nu V^\nu(1) + V^\sigma(2d) = \lambda V^\sigma(2d). \tag{2.6c}$$

With the help of the substitution method the equations (2.6) can be reduced to the matrix equation

$$(\lambda - 1)\lambda^{2d-1} V^\sigma(1) = \sum_{\nu=1}^k z_\nu \left[1 + (\lambda - 1) \sum_{j=1}^d w_{\sigma\nu}(j)\lambda^{d-j} \right] V^\nu(1). \tag{2.7}$$

This equation has a non-trivial solution if $V^\sigma(1) \neq 0$. Then the solution of (2.7) can be found with the help of the determinant equation

$$\det(m(\lambda) - (\lambda - 1)\lambda^{2d-1}) = 0 \tag{2.8}$$

where the elements of the matrix m are defined as

$$m^{\sigma\nu}(\lambda) = \left[1 + (\lambda - 1) \sum_{j=1}^d w_{\sigma\nu}(j)\lambda^{d-k} \right] z_\nu. \tag{2.9}$$

We are interested in the continuum limit $d \to \infty$ ($d_0 \to 0$) but under the condition that the rod length $s = dd_0$, the density of σ-rods and the interaction ranges have the constant values during the limiting procedure. In this limit one can find the continuum equation of state

$$\beta P s = \lim_{d \to \infty} d \ln \lambda \tag{2.10}$$

after the thermodynamic limit has been calculated, where P means the pressure per rod, β is the inverse temperature and λ corresponds to the maximum eigenvalue of the transfer matrix M (in the thermodynamic limit $Q_L \sim \lambda_{max}^L$). In the continuum the natural unit of length for the model is the rod size $s = 1$. Therefore we introduce the following scaling procedure

$$\lambda^d \to \lambda \tag{2.11a}$$

$$z_\nu d \to z_\nu. \tag{2.11b}$$

The first scaling follows directly from (2.10) and, together with the other one, is consistent with the well known thermodynamic relation

$$\rho_\sigma = \left(\frac{z_\sigma}{\lambda} \right) \frac{d\lambda}{dz} \bigg|_{\lambda_{max}} \tag{2.12}$$

where the density ρ_σ is the mean number of the σ-rods per rod size. The scaling (2.11b) is necessary to have a finite chemical potential in (2.8) after the continuum limit. In the continuous case the matrix (2.9) reads as

$$m^{\sigma\nu}(\lambda) = \left[1 + \ln \lambda \int_0^1 w_{\sigma\nu}(x)\lambda^{1-x} \, dx \right] z_\nu. \tag{2.13}$$

One can find an analogous equation to (2.8) for the k-component mixture in [5]. In further considerations we make the simplifying assumption that the interaction $J_{\sigma\nu}(x)$ is constant in the range $x < s$ of the interaction and zero beyond it. We also restrict ourselves to the case of the two-component gas consisting of rods, say A and B. Then the expression (2.13) reduces to the form

$$m^{\sigma\nu}(\lambda) = [1 + (\lambda - 1)w_{\sigma\nu}]z_\nu \qquad (2.14)$$

and the condition (2.8) leads to the following equation

$$\lambda^4 (\ln \lambda)^2 - z_A a \lambda^2 \ln \lambda - z_B b \lambda^2 \ln \lambda + z_A z_B (c^2 - ab) = 0 \qquad (2.15)$$

after performing the scaling (2.11) and the limit $d \to \infty$, where

$$a = 1 + (\lambda - 1)w_{AA} \qquad (2.16a)$$

$$b = 1 + (\lambda - 1)w_{BB} \qquad (2.16b)$$

$$c = 1 + (\lambda - 1)w_{AB}. \qquad (2.16c)$$

With the help of (2.15) and the thermodynamic relation (2.12) for the density of rods A and B we can exclude the chemical potentials. To this end we differentiate (2.15) with respect to z_A and z_B and we obtain two other equations

$$2\rho_A \lambda^4 \ln \lambda (2 \ln \lambda + 1) - z_A \{\rho_A \lambda^2 [a(2 \ln \lambda + 1) + a'\lambda \ln \lambda] + a\lambda^2 \ln \lambda\}$$
$$- z_B \rho_A \lambda^2 (b(2 \ln \lambda + 1) + b'\lambda \ln \lambda)$$
$$+ z_A z_B \{(c^2 - ab) - \rho_A \lambda [ab' + ba' - 2cc']\} = 0 \qquad (2.17a)$$

$$2\rho_B \lambda^4 \ln \lambda (2 \ln \lambda + 1) - z_B \{\rho_B \lambda^2 [b(2 \ln \lambda + 1) + b'\lambda \ln \lambda] + b\lambda^2 \ln \lambda\}$$
$$- z_A \rho_B \lambda^2 (a(2 \ln \lambda + 1) + a'\lambda \ln \lambda)$$
$$+ z_A z_B \{(c^2 - ab) - \rho_B \lambda [ab' + ba' - 2cc']\} \qquad (2.17b)$$

for the unknown z_A and z_B, where prime denotes the derivative with respect to λ. After some tedious calculation the elimination of z_A and z_B from the equations can be done and we obtain the following equation of state

$$\beta Ps = \frac{\rho_A + \rho_B}{1 - (2 - \lambda a'/a)\rho_A - (2 - \lambda b'/b)\rho_B - \dfrac{2\lambda(a'/a + b'/b - 2c'/c)\rho_A\rho_B}{\rho_A + \rho_B + ((\rho_A - \rho_B)^2 + 4(ab/c^2)\rho_A\rho_B)^{1/2}}}. \qquad (2.18)$$

We want to stress that although we have assumed constant interaction the equation remains the same for the general short-range interaction potential. Let us note that in the limit $\rho_B \to 0$ one obtains the Takahashi equation of state for the one-component gas [6] and the ideal gas equation of state once the interactions between the rods vanish. In general, the ideal k-component gas equation of state reads as

$$\beta Ps = \sum_{\sigma=1}^{k} \rho_\sigma \left(1 - \sum_{\sigma=1}^{k} \alpha_\sigma \rho_\sigma\right)^{-1} \qquad (2.19)$$

where α_σ are the rod sizes.

The right-hand side of (2.18) depends on the pressure, because $\lambda = e^{\beta P s}$. However, one can easily examine the equation numerically, in particular the isobars. The ground state densities of the system subject to a constant pressure can be found exactly.

3. Discussion of the results

In the previous section we have derived the equation of state (2.18) for a short-range interacting two-component gas of rods having the same size. Analogously to that case one can express (2.8) in terms of the densities for the k-component mixture. We are interested in the case when the system of rods is subject to a constant pressure. It is known that this type of condition can lead to water-like properties for some models with repulsive interactions [3], where even in one space dimension one can expect a kind of phase transition governed by the pressure factor. Therefore we restrict our considerations to the discussion of isobars and ground state properties of (2.18).

The most interesting behaviour of the gas of particles A and B occurs when all interactions J_{AA}, J_{BB} and J_{AB} are repulsive (<0). Although the interactions are short-range the ground state portrait becomes very complicated. In figure 1 we divided the space of the interaction parameters J_A, J_B and J_{AB} into eight typical regions according to the reaction of the gas to the applied pressure. Figures $2(a)$–(e) show the ground state densities behaviour of the system of rods A and B in these regions. In each case increasing pressure makes structural changes in the gas, collapsing it finally into a uniformly dense structure. The numbers which label the isobars grow with increasing pressure. The solid lines correspond to the ground states, which are stable with respect to the value of the applied pressure, while the dashed lines describe the unstable states. However, the states which are unstable with respect to the pressures are stable against the temperature changes. It is evident from figure 3 where the plots of ρ_A and ρ_B are made for the unstable case. For completeness in figure 4 we show how the isobars share their phase space in non-zero temperature. It is evident from figures $2(a)$–(e) that in the model with short-range repulsive interactions there are at most seven possible ground states. The number of states diminishes when the attractive interactions between
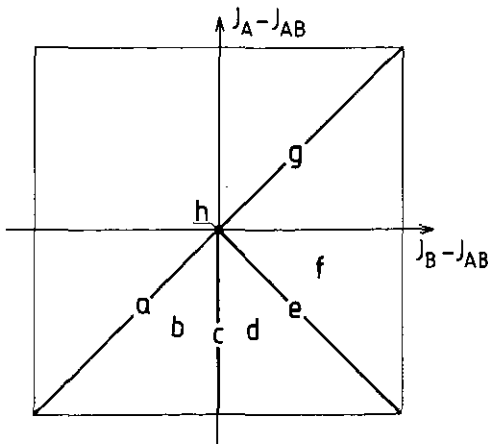

Figure 1. Division of the interaction parameter space into eight characteristic regions a–h with respect to the response of the gas to the applied pressure.
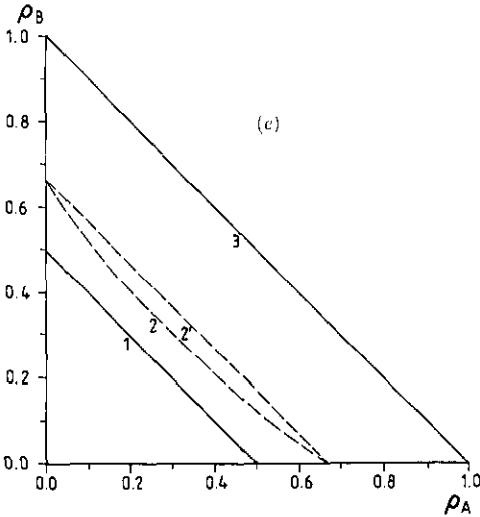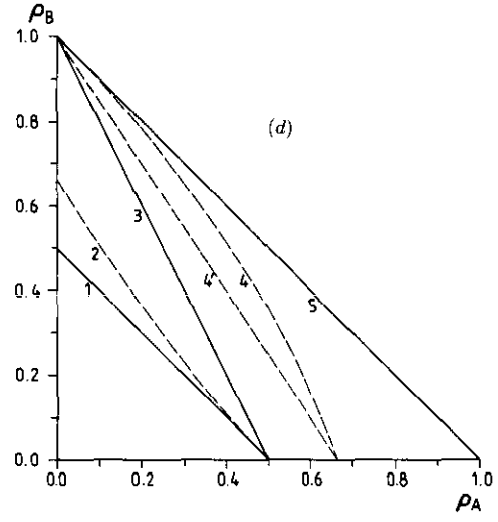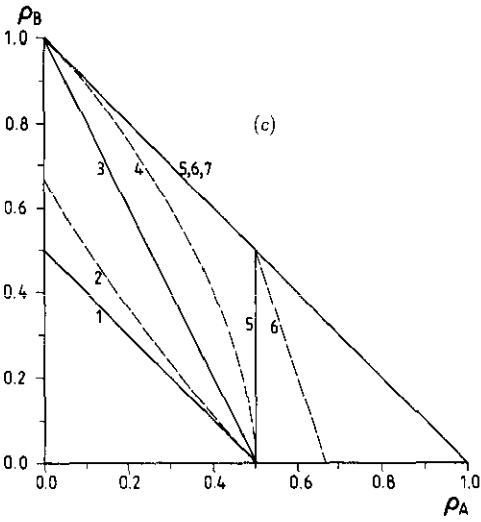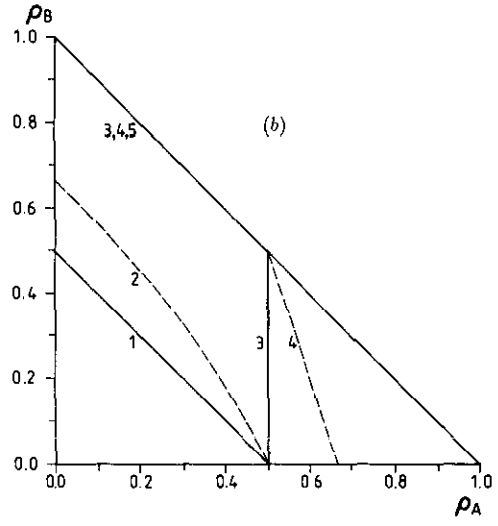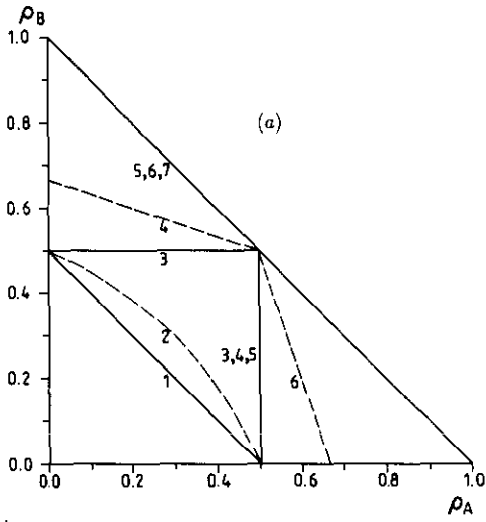
Figure 2. Ground state densities for the gas subject to constant pressure in (*a*) region b (if the isobar 5 and the upper branch of the isobar 6 vanish then also region a); (*b*) region c; (*c*) region d; (*d*) region e with the isobars 1, 2, 3, 4 and region f where the isobar 4' is substituted for 4; (*e*) region g with the isobars 1, 2, 3 and region h with the isobars 1, 2', 3.
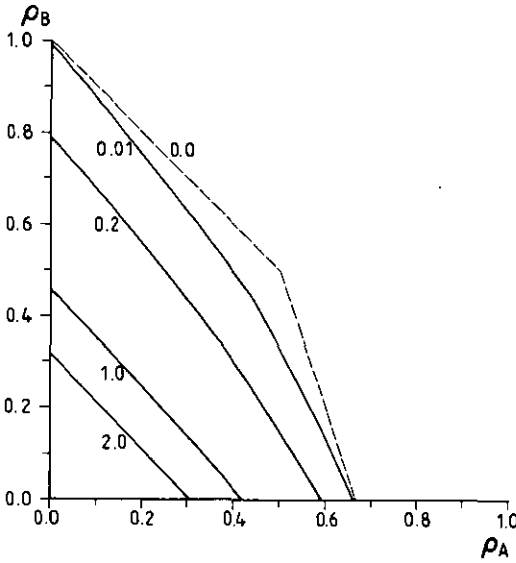
Figure 3. Isobars in the unstable region c of figure $2(b)$ for the temperatures $\tau = 2.0$, 1.0, 0.2, 0.01, 0, where $\tau = k_B T/|J_A|$ and $sP/|J_A| = 1.0$, $J_A/|J_A| = -1$, $J_2/|J_A| = -0.5$, $J_{AB}/|J_A| = -0.5$.
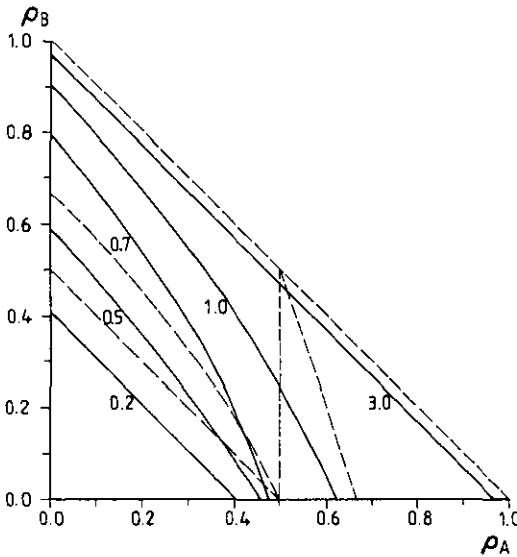

Figure 4. Isobars corresponding to the pressure $P/|J_A| = 0.2$, 0.5, 0.7, 1.0, 3.0 for the temperature $\tau = 0.1$ and the interaction parameters defined as in figure 3.

the rods are present. In particular, they reduce to the one ground state $\rho_A + \rho_B = 1$ if all interactions become attractive. One can easily imagine how complicated the behaviour of the system could be if the interaction between the rods had depended on the range of the interaction. For example, the one-dimensional short-range inter-action potential with the repulsive and attractive part can produce three ground states even for a one-component fluid [3, 7].

4. Conclusions

We have presented the transfer matrix method for the continuum k-component gas of interacting rods. In the particular case of two sorts of gas particles, A and B, we have discussed their equation of state when the system is subject to constant pressure. In the model, each gas component is nothing but the Takahashi gas [6]. Our method is based on the approach of Shulepov and Aksenenko [2] who applied the transfer matrix language of the lattice gas to the continuum case. The matrix method is an alternative to the traditional approach with the help of the Laplace transform for the partition function [8]. The generalization of the method to further-range interacting gases is possible. In particular, the inclusion of the infinite range interactions between the rods (mean field approximation) results in the van der Waals type of the equation of state adjusted by the exact structure of the right-hand side of (2.18).

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