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Mean-field state equations of multicomponent and multiphase systems

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Starting with an application of the mean-field approximation to a general classical *compound-lattice model* which is built up by an arbitrary number of sublattices, state equations are derived. A further improvement of this model achieved in such a way that an increasing number of sublattices are considered leads to models which become more and more picture true to nature. Finally the transition to a certain *continuum model* is performed, yielding a coupled set of nonlinear integral equations for the one-particle density distribution functions of a three-dimensional system consisting of continuously movable classical particles of N different species which interact by very general two-body interactions. The thermal expansion of a possible crystalline structure of the continuum model is described by an additional transcendental state equation.

I. INTRODUCTION

Mean-field approximations have been applied to order-disorder phenomena for the first time by Weiss[1] and Bragg and Williams.[2] Weiss used such approximations for his famous "Weiss model" of ferromagnetism. Bragg and Williams considered them in connection with their theory of order-disorder transitions of binary alloys. Since Lee and Yang[3] discovered the formal connection between the Ising model of ferromagnetism and the lattice-gas model of fluid systems, the mean-field approximation became a basic first-order approximation in the statistical-thermodynamical theory of fluids. A general discussion of these topics can be found in the books of Brout[4] and Münster.[5]

Recently, mean-field approximations have been applied to refined cell models of crystal-liquid systems,[6] and compound-lattice models of certain allotropes.[7] In these cases,[6,7] the phenomenon of the maximum of the melting curve in the pressure-temperature phase diagram could be cleared up. Realistic structural solid-solid phase transitions have been found[7] with pressure-temperature phase diagrams similar to that of Cs. Some hard-core lattice models with arbitrary soft interaction tails have been treated with a combined mean-field and cluster-variation approximation.[8] Realistic inert-gas-like phase-transition curves of a gas-liquid-solid system and also solid-solid structural transitions of an allotropic gas-liquid-solid-solid system could be proved there. Cell models which are related in some way to the lattice models have been treated by similar methods delivering also similar results.[12-17] Finally, the spinoidal isotherms, critical lines, and double plait points of a lattice model of a binary fluid mixture have been calculated in mean-field approximation.[9,10] A great deal of characteristic phenomena such as azeotropy, gas-gas and liquid-liquid immiscibility are well understood and described in comparatively good agreement with experimental results.[10]

A critical consideration of all the above-mentioned results obtained in mean-field approximation suggests that the mean-field approximation succeeds in outlining the main features of the equilibrium and phase-transition behavior of simple and more complex thermodynamical systems. It further appears to be a good first-order approximation and an appropriate starting point for more exact quantitative calculations.

Encouraged by these results, it seems reasonable to use an application of the mean-field approximation to general and realistic lattice or continuum models of real multiphase and multicomponent systems.

II. MODELS

In this paper one *compound-lattice model* and one *continuum model* are considered, which may be described in the following:

We suggest classical particles of N different species without any internal degrees of freedom moving in a three- (or two-) dimensional space. These particles may interact by arbitrary two-body particle interactions composed of *very small* hard core and added soft interaction tails. The shape of the hard-core cell can be variable, but it should be equivalent with that of the unit cell of an arbitrary Bravais lattice ("variable hard core"). The soft interaction tails may be represented by integrable potential functions $-v_{ij}^*$ with existent Fourier transform. The functions $-v_{ij}^*$ may be zero for pairs of particles within the hard-core cell and may coincide otherwise with arbitrary integrable potential functions $-v_{ij}(|\vec{r}_{ij}|)$ with existent Fourier transforms which depend only on the distance $|\vec{r}_{ij}|$ between the two particles of species i and j and have steady differential derivatives in the whole coordinate space and become positive infinite at the origin. The origin is assumed to lie in the midst of the hard-core cell. Although the shape of the hard core is somewhat arbitrary in the sense mentioned above, the volume of all considered hard-core cells should be equal to unit volume v. The volume v of the hard-core cells should be so small that $-v^*_{ij}$ at the edges of the cells assumes very large positive values that particle number densities on lattice sites can be replaced in a reasonable way by real particle volume densities, and that the variation of v^*_{ij} within the range of a hard-core diameter is extremely small.

By utilizing principles of integral calculus it seems to be reasonable then to assume that the evaluation of the configurational part of the grand canonical partition function is comparatively independent of the specially chosen hard-core cell and coordinate net in the domain of integration provided that the lattice constants of such nets are small enough. The lower-bound of the lattice constants is thereby given by the magnitude of the hard-core cell. It is therefore useful to choose simple regular periodical point lattices with equal numbers of lattice sites (that is equal to volume v per lattice site, where v is the volume of the hard-core cell) as coordinate nets in the domain of integration. In the three-dimensional space the only possible types of such lattices are the 14 Bravais lattices. The advantage of these lattices is that not only the configurational integral in the grand canonical partition function can be replaced by a sum over all configurations on these lattices, but also that all possible homogeneous fluid and all possible periodical crystalline particle density structures can be described in a sufficient way.

While a homogeneous fluid structure is simply represented by a homogeneous number density distribution on the lattice, the number of particles per lattice site remains a description of a crystalline structure somewhat more complicated. If a crystalline structure with the periodicity of a special Bravais lattice is to be described, one has to first construct the corresponding *compound lattice*:

For this reason one chooses a Bravais lattice of the same type, but with a much smaller unit cell (the hard-core cell) as a basic lattice. Afterwards, a greater number of unit cells of the basic lattice will be joined to a real unit cell of the given periodical structure of the same Bravais type. (This is possible when the ratios of the edge lengths of the unit cells of the real periodical structure and the basic lattice are integers.) The lattice sites in the real unit cell can then be considered as coordinate points of a coordinate system with an origin in the midst of the real cell, and coordinate axes parallel to the three vectors which span up the real unit cell. As coordinates of a point in the real unit cell, the Weiss indices can then be used. It is always possible in the case of the Bravais lattices to find simple rectangular- or oblique-angled coordinate systems of this kind even in the case of the hexagonal lattice.[11] In a somewhat different interpretation, the basic lattice can be considered a composition of a great number of shifted equivalent sublattices with the real unit cell of the given periodic structure as the unit cell in such a way that each lattice point in the real unit cell belongs to a different sublattice. Of course, lattice sites on opposite faces of the real unit cell are only counted once. The composed lattice, described in a general way above, may be denoted *compound lattice*. An example is illustrated in Fig. 1.

In Fig. 1, a section of a plane square compound lattice composed of four equivalent sublattices is shown. One representative real unit cell of the periodical structure is drawn with heavy solid lines. In the midst of this unit cell, the origin of the coordinate system is drawn as an unfilled circle. The filled circles are equivalent coordinate points belonging to the different sublattices.

After having defined the compound lattice of a given Bravais type it is now possible to describe every corresponding periodical particle density distribution: Considering an ensemble of com-

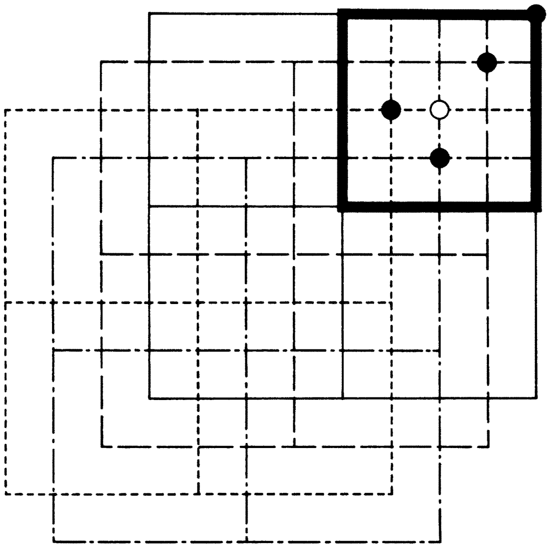

FIG. 1. Section of a plane square compound lattice composed of four equivalent sublattices: solid line represents the sublattice with Weiss index coordinates (-2, 2); broken line represents the sublattice with Weiss index coordinates (-1, 1); dotted line represents the sublattice with Weiss index coordinates (0,-1); and line composed of alternate dots and dashes represents the sublattice with Weiss index coordinates (1, 0).

pound lattices, one needs only distribute the particles with homogeneous number densities on the sublattices, whereby the homogeneous sublattice densities vary from sublattice to sublattice. *If the ratios of the sublattice densities of the various particle species are constant for all sublattices, the periodical density distribution of a completely disordered crystalline mixture is described. If these density ratios vary from sublattice to sublattice in a way that on some different sublattices the densities of different particle species become maximum, the periodical density distribution of an ordered crystalline mixture (super structure) is reproduced.*

The so-called compound-lattice model which will be considered in this paper consists now of the system of classical particles with pair interaction as defined above which moves on all (Bravais-type) possible compound lattices.

It is obvious that this compound-lattice model becomes an increasingly realistic picture of real multiphase and multicomponent systems if the number of lattice sites of the possible basic lattices is increased while the total volume of the system is simultaneously kept fixed. When the volume v of the unit cell of the basic lattice that is the volume of the hard-core cell becomes small enough so that summations can be replaced by integrations and the number densities (particles per lattice site) can be replaced by ordinary densities (particles per volume unit), then one approaches the continuum model where the particles in contrast to the lattice model can be shifted continuously through the space. This model will be also considered in the paper. It may be supplemented that thermal expansion of a crystal is described by both models.

III. MEAN-FIELD STATE EQUATIONS

A. Compound-lattice model

According to the general description of our models in Sec. II, an arbitrary compound lattice may be globally denoted by an index BT indicating the Bravais type of basic lattice, the unit cell volume v of the basic lattice, and the volume V_E^{BT} of the real unit cell of the compound lattice. The complete notation is achieved by denoting the sublattices by integer triples n_1, n_2, n_3 (the Weiss index coordinates of the sublattice points in a unit cell of the compound lattice) which may be represented by a vector $\vec{\mathrm{n}}$. They are restricted to the semiopen domains $[-\alpha_1,\alpha_1)$, $[-\alpha_2,\alpha_2)$, $[-\alpha_3,\alpha_3)$, where α_1, α_2, α_3 depend on V_E^{BT}. The α triplet may also be represented by a vector denoted $\vec{\alpha}$. The homogeneous sublattice densities of particles of species i on the sublattice $\vec{\mathrm{n}}$ which characterize a periodical particle distribution on the compound lattice may be denoted $\rho_i(\vec{\mathrm{n}})$. They are the fundamental macroscopic variables of our model.

The evaluation of the grand canonical partition function Ξ of the compound-lattice model in mean-field approximation now means in our picture that Ξ is approximated by three steps.

In the *first step*, Ξ is replaced by

$$\Xi \approx \sum_{\mathrm{BT}} \sum_{V_E^{\mathrm{BT}}} \frac{1}{Z}\left[\sum_{\{\rho_1(\vec{\mathrm{n}})\}} \cdots \sum_{\{\rho_N(\vec{\mathrm{n}})\}} W_{\mathrm{conf}}(V_E^{\mathrm{BT}}) \exp[-\beta V\langle\mathcal{E}(V_E^{\mathrm{BT}})\rangle] \exp\left[\beta V \sum_{i=1}^{n}\left(\sum_{\vec{\mathrm{n}}} g(\vec{\mathrm{n}})\rho_i(\vec{\mathrm{n}})\right)\mu_i\right]\right],$$

where Z is the number of all possible compound lattices for *fixed* v, V is the total number of lattice sites on the basic lattice, $g(\vec{\mathrm{n}})$ is the sublattice site distribution function that is the ratio of the number of lattice sites on the sublattice $\vec{\mathrm{n}}$ to V, N is the number of different species of particles, μ_i is the chemical potential of the particle species i, β is the reciprocal of kT with k the Boltzmann constant and T the absolute temperature, $W_{\mathrm{conf}}(V_E^{\mathrm{BT}})$ is the number of all configurations with fixed sublattice densities $\rho_i(\vec{\mathrm{n}})$ and $\langle\mathcal{E}(V_E^{\mathrm{BT}})\rangle$ is the mean configurational energy of the compound-lattice model on the compound lattice with indices BT, V_E^{BT}. The sum symbols $\sum_{\{\rho_i(\vec{\mathrm{n}})\}}$ in the Ξ expression above are abbreviations for the multiple sums

$$\sum_{\rho_i(\vec{\mathrm{n}}_1)=0}^{1} \sum_{\rho_i(\vec{\mathrm{n}}_2)=0}^{1} \cdots \sum_{\rho_i(\vec{\mathrm{n}}_\nu)=0}^{1},$$

where $\vec{\mathrm{n}}_1, \ldots, \vec{\mathrm{n}}_\nu$ are all sublattice indices.

In the *second step*, $\langle\mathcal{E}(V_E^{\mathrm{BT}})\rangle$ is approximated by a quadratic function of the sublattice densities which is, apart from sign, identical with that term standing in the first bracket of Eq. (1). This means that any pair correlation and higher correlations are neglected.

Finally, in the *third step* the approximated partition sum above is replaced by its maximum term. Inserting this approximated Ξ in the fundamental statistical formula

$$p = (1/\beta)(1/V)\ln\Xi$$

yields the pressure-density function (1) (where p is the pressure), because Z is proportional to V and cancels in the thermodynamic limit:

$$pv=\frac{1}{2}\left(\sum_{i,\,j=1}^{N}\sum_{\vec{\mathrm{m}}}^{\vec{\alpha}(V_E^{\mathrm{BT}})}\sum_{\vec{\mathrm{n}}}^{\vec{\alpha}(V_E^{\mathrm{BT}})} g(\vec{\mathrm{m}})\,w_{ij}(\vec{\mathrm{m}},\vec{\mathrm{n}}:V_E^{\mathrm{BT}})\rho_i(\vec{\mathrm{m}})\rho_j(\vec{\mathrm{n}})\right)+\sum_{i=1}^{N}\left(\sum_{\vec{\mathrm{m}}}^{\vec{\alpha}(V_E^{\mathrm{BT}})} g(\vec{\mathrm{m}})\rho_i(\vec{\mathrm{m}})\right)\mu_i+\frac{1}{\beta V}\ln[W_{\mathrm{conf}}(V_E^{\mathrm{BT}})]\,. \tag{1}$$

The sum symbols $\sum_{\vec{\mathrm{m}}}^{\alpha(V_E^{\mathrm{BT}})}$ in (1) and throughout the paper are abbreviations for the multiple sums

$$\sum_{m_1=-\alpha_1}^{\alpha_1-1}\sum_{m_2=-\alpha_2}^{\alpha_2-1}\sum_{m_3=-\alpha_3}^{\alpha_3-1}\,,$$

where α_i are given by the Bravais type BT and V_E^{BT}.

The terms $w_{ij}(\vec{\mathrm{m}},\vec{\mathrm{n}};V_E^{\mathrm{BT}})$ in (1) are the interaction sums

$$w_{ij}(\vec{\mathrm{m}},\vec{\mathrm{n}};V_E^{\mathrm{BT}})=\sum_{\vec{\mathrm{x}}}^{(\vec{\mathrm{m}},\vec{\mathrm{n}})} v_{ij}(|\vec{\mathrm{y}}-\vec{\mathrm{x}}|)\,, \tag{2}$$

where $-v_{ij}(|\vec{\mathrm{y}}-\vec{\mathrm{x}}|)$ is the particle interaction potential between two particles of species i and j at space points $\vec{\mathrm{y}}$ and $\vec{\mathrm{x}}$, respectively. In the sum (2), $\vec{\mathrm{y}}$ is the space vector of a fixed arbitrary site on sublattice $\vec{\mathrm{m}}$, while $\vec{\mathrm{x}}$ is the space vector of a running site which covers all sites on sublattice $\vec{\mathrm{n}}$ which are not identical with $\vec{\mathrm{y}}$. From (2) it follows directly that the function $w_{ij}(\vec{\mathrm{m}};\vec{\mathrm{n}};V_E^{\mathrm{BT}})$ is symmetric in the indices i and j and in the indices $\vec{\mathrm{m}}$ and $\vec{\mathrm{n}}$. In the case $\vec{\mathrm{m}}=\vec{\mathrm{n}}$, the function becomes independent of the $\vec{\mathrm{m}}$.

The number of all configurations with fixed sublattice densities $W_{\mathrm{conf}}(V_E^{\mathrm{BT}})$ on the compound lattice which is denoted by BT and V_E^{BT} is a comparatively simple combinatorial expression:

$$W_{\mathrm{conf}}(V_E^{\mathrm{BT}})=\prod_{\vec{\mathrm{m}}}^{\vec{\alpha}(V_E^{\mathrm{BT}})}\left\{[g(\vec{\mathrm{m}})V]!\Big/\prod_{i=1}^{N}[\rho_i(\vec{\mathrm{m}})g(\vec{\mathrm{m}})V]!\right.$$
$$\left.\times\left[\left(1-\sum_{i=1}^{N}\rho_i(\vec{\mathrm{m}})\right)g(\vec{\mathrm{m}})V\right]!\right\}. \tag{3}$$

The production symbol $\prod_{\vec{\mathrm{m}}}^{\alpha(V_E^{\mathrm{BT}})}$ in (3) is an abbreviation for the multiple product

$$\prod_{m_1=-\alpha_1}^{\alpha_1-1}\prod_{m_2=-\alpha_2}^{\alpha_2-1}\prod_{m_3=-\alpha_3}^{\alpha_3-1}\,,$$

where the α_i are again given by the Bravais type BT and V_E^{BT}.

Taking the thermodynamic limit $V\to\infty$, the logarithm of $W_{\mathrm{conf}}(V_E^{\mathrm{BT}})$ can be easily evaluated with the aid of Stirling's formula. The result can be inserted in (1), giving the following complete mean-field pressure density relation of a given Bravais-type periodical structure BT, V_E^{BT}:

$$pv=\sum_{\vec{\mathrm{m}}}^{\vec{\alpha}(V_E^{\mathrm{BT}})} g(\vec{\mathrm{m}})\left\{\frac{1}{2}\left(\sum_{i,\,j=1}^{N}\sum_{\vec{\mathrm{n}}}^{\vec{\alpha}(V_E^{\mathrm{BT}})} w_{ij}(\vec{\mathrm{m}},\vec{\mathrm{n}};V_E^{\mathrm{BT}})\rho_i(\vec{\mathrm{m}})\rho_j(\vec{\mathrm{n}})\right)+\sum_{i=1}^{N}\rho_i(\vec{\mathrm{m}})\mu_i\right.$$
$$\left.-\frac{1}{\beta}\left[\left(1-\sum_{i=1}^{N}\rho_i(\vec{\mathrm{m}})\right)\ln\left(1-\sum_{i=1}^{N}\rho_i(\vec{\mathrm{m}})\right)+\sum_{i=1}^{N}\rho_i(\vec{\mathrm{m}})\ln[\rho_i(\vec{\mathrm{m}})]\right]\right\}. \tag{4}$$

The sublattice densities $\rho_i(\vec{\mathrm{m}})$ in (4) must be chosen in the way that p becomes a maximum, that is, p must be differentiated with respect to them. This delivers the following set of coupled transcendental mean-field state equations for a given Bravais structure BT, V_E^{BT}:

$$\rho_i(\vec{\mathrm{m}})\Big/\left(1-\sum_{j=1}^{N}\rho_j(\vec{\mathrm{m}})\right)=\exp\left[\beta\left(\sum_{j=1}^{N}\sum_{\vec{\mathrm{n}}}^{\vec{\alpha}(V_E^{\mathrm{BT}})} w_{ij}(\vec{\mathrm{m}},\vec{\mathrm{n}};V_E^{\mathrm{BT}})\rho_j(\vec{\mathrm{n}})+\mu_i\right)\right]\,,\quad i=1,\cdots,N;\ \vec{\mathrm{m}}\subset V_E^{\mathrm{BT}} \tag{5}$$

together with the thermodynamic relation

$$\frac{\partial p}{\partial\mu_i}=\sum_{\vec{\mathrm{m}}}^{\vec{\alpha}(V_E^{\mathrm{BT}})} g(\vec{\mathrm{m}})\rho_i(\vec{\mathrm{m}})=\rho_i\,, \tag{6}$$

where ρ_i is the mean density of the particle species i.

B. Continuum model

When the lattice constants of the basic lattices of the various Bravais types and therefore the hard-core cell volume v is chosen small enough, the discontinuous Weiss index coordinates $\vec{\mathrm{m}}$ in the unit cell can be replaced by continuous Cartesian coordinates $\vec{\mathrm{x}}$ or more appropriately by oblique-angled coordinate systems corresponding to the Bravais type of the lattice.[11] The sums $\sum_{\vec{\mathrm{m}}}^{\vec{\alpha}(V_E^{\mathrm{BT}})}$ over the unit cell V_E^{BT} can then be replaced by integrations $(1/v)\int_{V_E^{\mathrm{BT}}}d\tau$ in Cartesian coordinates $\vec{\mathrm{x}}$, or more appropriately in oblique-angled coordinates $\vec{\mathrm{x}}'$. Using the new coordinates lying in the semiopen intervals $-\alpha e_1\le x_1'<\alpha e_1$, $-\alpha e_2\le x_2'<\alpha e_2$, $-\alpha e_3\le x_3'<\alpha e_3$, where $[-e_1,e_1)$, $[-e_2,e_2)$, $[-e_3,e_3)$ are the semiopen domains of the unit cell V_E^{BT} with unit volume; then the integration $\int_{V_E^{\mathrm{BT}}(\alpha)} d\tau$ is an abbreviation of threefold integration

$$\int_{-\alpha e_1}^{\alpha e_1}\int_{-\alpha e_2}^{\alpha e_2}\int_{-\alpha e_3}^{\alpha e_3} \frac{\partial(\vec{x})}{\partial(\vec{x}')}dx_1'dx_2'dx_3' ,$$

where $\partial(\vec{x})/\partial(\vec{x}')$ is the functional determinant of the transformation $\vec{x}\rightarrow\vec{x}'$. This abbreviation shall be considered in the following formula of the continuum model, especially in (7) and (8). The real positive number α is a true measure of the magnitude of the unit cell, because its volume $V_E^{\mathrm{BT}}(\alpha)$ is simply α^3 owing to the definition of α. If one carries out the summation in (2) for continuous coordinates, one has to be certain that v_{ij} is replaced by v_{ij}^*. Terms due to space points pairs lying in the same hard-core cell are then not counted, as demanded. If one considers that $g(\vec{m}) = v/V_E^{\mathrm{BT}}$ and further replaces the number densities by real (particles per volume) densities [whereby the connections $V^{(V)}(\vec{n}) = vV^{(N)}(\vec{n})$,

$$\rho_i^{(N)}(\vec{n}) = \frac{N_i(\vec{n})}{V^{(N)}(\vec{n})} = \frac{vN_i(\vec{n})}{V^{(V)}(\vec{n})} = v\rho_i^{(V)}(\vec{n})$$

between v, the volume $V^{(V)}(\vec{n})$, the number $N_i(\vec{n})$ of particles of species i, the number of lattice sites $V^{(N)}(\vec{n})$, the number density $\rho_i^{(N)}(\vec{n})$ of species i, and the volume density $\rho_i^{(V)}(\vec{n})$ of species i all belonging to sublattice $\vec{n}$ must be considered], then the pressure-density relation (4) of the compound-lattice model changes into that of the continuum model:

$$pV_E^{\mathrm{BT}}(\alpha) = \frac{1}{v}\int_{V_E^{\mathrm{BT}}(\alpha)} d\vec{y}\left\{\frac{1}{2}\left(\sum_{i,j=1}^{N}\frac{1}{v}\int_{V_E^{\mathrm{BT}}(\alpha)} d\vec{x}\, w_{ij}(\vec{y}-\vec{x}; v, V_E^{\mathrm{BT}}(\alpha))[v\rho_i(\vec{y})][v\rho_j(\vec{x})]\right) + \sum_{i=1}^{N}[v\rho_i(\vec{y})]\mu_i \right.$$
$$\left. - \frac{1}{\beta}\left[\left(1-\sum_{i=1}^{N}[v\rho_i(\vec{y})]\right)\ln\left(1-\sum_{i=1}^{N}[v\rho_i(\vec{y})]\right) + \sum_{i=1}^{N}[v\rho_i(\vec{y})]\ln[v\rho_i(\vec{y})]\right]\right\}. \qquad (7)$$

In (7), apart from the explicit macroscopic variables $\rho_i(\vec{x})$, the additional implicit macroscopic variable α as a thermal expansion parameter occurs. Again, these variables must be chosen in such a way that the pressure function (7) of the continuum model becomes maximum. This leads to the following coupled set of nonlinear integral equations:

$$\ln\left[v\rho_i(\vec{y})\Big/\left(1-\sum_{j=1}^{N}v\rho_j(\vec{y})\right)\right] = \beta\left(\sum_{j=1}^{N}\frac{1}{v}\int_{V_E^{\mathrm{BT}}(\alpha)} d\vec{x}\, w_{ij}(\vec{y}-\vec{x}; v, V_E^{\mathrm{BT}}(\alpha))[v\rho_j(\vec{x})] + \mu_i\right),$$
$$i = 1, \ldots, N;\ \vec{y}\subset V_E^{\mathrm{BT}}(\alpha), \qquad (8)$$

which are the continuum analogs of (5). For simplicity, the volume density $\rho_i^{(V)}(\vec{x})$ in (7) and (8) is denoted by $\rho_i(\vec{x})$. Concerning the range of validity of the Eqs. (7) and (8), it can be stated that they are only reasonable for small but finite hard-core volume v. If v becomes smaller and smaller (7) and (8) approach closer to the corresponding state equations (4) and (5) of the compound-lattice model. In the limit $v\rightarrow 0$, however, (7) and (8) become irrelevant, because the volume density $\rho_i^{(V)}(\vec{n})$ is then defined in this limit on a point set with zero measure, which is inappropriate for a real volume density. The number density $\rho_i^{(N)}(\vec{n})$, for the same reason, cannot approach a real volume density which would be the appropriate probability distribution function in this limit. Therefore, (4) and (5) also become irrelevant for $\lim v = 0$. In order to construct a real volume density in the limit $v\rightarrow 0$, it is necessary to take for finite v the mean value of the volume densities $\rho_i^{(V)}(\vec{x})$ of all such sublattice points $\vec{x}$ lying in a small volume ΔV, whereby v tends to zero afterwards:

$$\rho_i^{(\mathrm{real})}(\vec{x}_{\Delta V}) = \lim_{v\rightarrow 0}\frac{1}{\Delta V}\sum_{\vec{x}}^{\Delta V} v\rho_i^{(V)}(\vec{x}),\quad \vec{x}_{\Delta V}\subset\Delta V.$$

This "real density," however, corresponds exactly to that volume density $\rho_i^{(V)}(\vec{x})$ belonging to the decomposition $v = \Delta V$. It is therefore clear that in the case of the continuum model (as well as in the case of the compound-lattice model), a finite hard-core volume v must be considered. The calculated results will be dependent on v for both models on account of (7), (8) and (4), (5), respectively. But while v in the case of the compound-lattice model can be chosen arbitrary in the case of the continuum model, v must be chosen so small (corresponding to the assumptions made in Sec. II) that the volume densities and interaction functions practically do not vary in v, so that all sums can be replaced by integrations independent of the shape of v.

The thermal expansion parameter α can be determined by a total variation of p in dependence on α. For this reason the solutions $\rho_i(\vec{x};\alpha)$ of (8) which are α dependent must be inserted in (7), giving, due to $V_E^{\mathrm{BT}}(\alpha) = \alpha^3$ a function $p = (1/\alpha^3) \times f(\alpha, v)$ for the pressure. $dp/d\alpha = 0$ gives then the transcendental equation

$$\alpha\frac{df(v,\alpha)}{d\alpha} = 3f(\alpha, v) \qquad (9)$$

for the determination of α which characterizes the thermal expansion in thermodynamical equilibrium.

Equations (7)–(9) represent the complete set of mean-field state equations of the continuum model. For the coupled set of integral equations (8), a representation in the $\vec{k}$ space of the reciprocal lattice is possible. Defining the function

$$f_i(\vec{x}) = \ln\left[v\rho_i(\vec{x}) \Big/ \left(1 - \sum_{j=1}^{N} v\rho_j(\vec{x})\right)\right],$$

which is of the same periodicity as the density $\rho_i(\vec{x})$ and the interaction sum $w_{ij}(\vec{y}-\vec{x}; v, V_E^{\mathrm{BT}}(\alpha))$, one obtains by a Fourier transform, considering the folding theorem, the following set of linear algebraic equations:

$$\frac{1}{\beta}\bar{f}_i(\vec{k}) - \mu_i\,\delta(\vec{k}) = V_E^{\mathrm{BT}}(\alpha) \sum_{j=1}^{N} \bar{w}_{ij}(\vec{k}) v\bar{\rho}_j(\vec{k}),$$

$$i = 1, \ldots, N \quad (10)$$

for the Fourier components $\bar{f}_i(\vec{k})$, $\bar{\rho}_i(\vec{k})$, and $\bar{w}_{ij}(\vec{k})$, whereby $\delta(\vec{k})$ is the Kronecker symbol.

Consider now that in the case of the hard-core continuum model in the interaction, sum v_{ij}^* must be used. As an ordinary Fourier transform $\bar{v}_{ij}^*(\vec{p})$ of v_{ij}^* exists in the $\vec{k}$ space of the reciprocal lattice; the following simple relation is valid:

$$\bar{w}_{ij}(\vec{k}) = [(2\pi)^3 / V_E^{\mathrm{BT}}]\,\bar{v}_{ij}^*(\vec{k}) . \quad (11)$$

For very small v, $\bar{v}_{ij}^*(\vec{k})$ in (11) can be replaced by the Fourier transform $\bar{v}_{ij}(\vec{k})$ of the soft interaction v_{ij}.

IV. DISCUSSION

Initially, a general description of the method of construction phase diagrams by use of the state equations (4), (5), and (7)–(9), respectively, may be given. In the case of the continuum model, Eq. (8) must first be solved. Afterwards, by insertion of the $\rho_i(\vec{x};\alpha)$ functions in (9), α is determined. Inserting α and $\rho_i(\vec{x};\alpha)$ into (7) for a given set of values of the chemical potentials μ_i, the pressure can be uniquely calculated for every type of a Bravais crystalline structure and, of course, for the fluid structures with homogeneous densities. As there is only a finite number of Bravais lattices that structure with the maximum pressure which corresponds to a stable phase can be easily selected. In this way a group of pressure faces of maximum pressure with the temperature $1/k\beta$ as group parameter can be uniquely constructed in the $(N+1)$-dimensional $(\mu_1, \ldots, \mu_N; p)$ space. Each point of these faces corresponds uniquely, for a given temperature, to a definite type of Bravais crystalline structure with a definite magnitude of the unit cell (characterized by α), and a definite corresponding periodical density distribution or, simply, to a fluid structure with definite homogeneous density. At the phase-transition points the faces of maximum pressure intersect for each temperature in $(N-1)$-dimensional hyperfaces of $(\mu_1, \ldots, \mu_N)$ space. In this way, all phase transition pressures and the corresponding phase-transition points in the $(N-1)$-dimensional hyperface of the $(\mu_1, \ldots, \mu_N)$ space can be determined for each temperature. Due to (8), two corresponding $(N-1)$-dimensional hyperfaces of coexisting densities in the $(\rho_1, \ldots, \rho_N)$ density space for each space point $\vec{x}$ are then simultaneously determined. In the case of the compound-lattice model, corresponding phase diagrams can be constructed in a completely analogous way with the only striking difference being the thermal expansion parameter α of a given Bravais-type unit cell cannot be calculated simply by an equation like (9). The magnitude of a unit cell of the compound lattice can be only determined by selecting among the whole set of possible integer triples $(\alpha_1, \alpha_2, \alpha_3)$ used in (1), (4), and (5) that triple where the pressure p in (4) becomes maximum. The mathematical treatment of the thermal expansion in the case of the compound-lattice model is therefore much more cumbersome than in the case of the continuum model.

What are now the main advantages and disadvantages of the models? At first it must be stated that the continuum model with finite v, as well as the compound-lattice model, is not a picture completely true to nature. The somewhat artificial "variable hard core" of this model cannot be suggested as a perfect alternative of real extended continuously shiftable hard cores with the shape of a sphere, or other shapes. The hard-core correlation of the continuum model is at most globally taken into account in the pure-mean-field approximation in the sense that at infinite pressures a collapse of the particles is prohibited, and a finite volume, namely, the proper volume of the particles is assumed. The influence of this lack on the mean-field results, however, vanishes more and more if the hard-core cell volume v becomes smaller and the interaction tends more and more to the soft core potential interaction $-v_{ij}$ defined at the beginning of Sec. II. On the other hand, the neglect of pair and higher correlations due to the soft-interaction tail can also entail that packing effects together with a corresponding variety of phases and phase diagrams are not described precisely enough. A more systematic consideration of the hard-core correlation is comparatively cumbersome, even in the case of simple hard-core lattice models.[8] Concerning the calculation of the equilibrium density distributions of a very refined compound lattice model, it can be stated that it is probably much more cumbersome than calculating the corresponding data of the continuum model. In the case of the compound-lattice model a set of a very large number of coupled transcendental equations (5) always must be solved. In the case of the continuum model, often only a set of a few coupled integral equations (8) must be solved. When allotropes are considered for each crystalline structure only one integral equation and (9) need to be solved, whereby the thermal expansion is automatically included. The evaluation of the pressure functions seems to be easier in the case of the continuum model (4) than in the case of the compound-lattice model (7). Unfortunately, it was not possible to develop a procedure of solving the system of integral equations (8). On the other hand, if the density distributions of all crystalline, and fluid structures of a real system are known from experiment in such a way that Fourier components can be calculated on account of (10) and (11), some statements can be given concerning the Fourier components of the soft-interaction tails $-v^*_{ij}$ and the complete interactions $-v_{ij}$. A reconstruction of the true interaction $-v_{ij}$ is perhaps then possible in some cases. As long as a solution of (8) cannot be given, it seems to be appropriate to calculate simple compound-lattice models consisting only of a few sublattices. Such models exhibit many of the characteristic thermodynamical features of real systems.[7] Especially if a symmetric density distribution in the unit cell is assumed, the number of coupled transcendental equations of the system (5) will severely be reduced. A numerical computer calculation then appears feasible. An entire judgment about the quality of the approximated models seems to be possible only by a treatment of a great number of various examples. In this sense, numerical calculations of (4), (5) and (7)-(9) for many different models may be tried in the future.

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