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Rigorous Treatment of the Liquid-Vapor Transition in a Polydisperse System with Kac Interaction

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Abstract Within the canonical formalism, we consider a polydisperse lattice-gas model and a polydisperse continuous system interacting with the Kac potential. We obtain rigorous expressions for free energy densities. We also exhibit phase diagrams of the bidisperse lattice-gas model.

Keywords Polydisperse lattice-gas model · Continuous polydisperse system · Kac potential · Liquid-vapor transition

1 Introduction

Polydisperse systems exhibit richer phase behavior than monodisperse systems and their phase diagrams become more complex [1]. Their coexisting states are less understood mathematically. In recent years, several models on polydispersity have been proposed and mathematical results have been obtained for some of them [2, 3]. Also, there are a number of studies associated with a glassy state, using numerical simulations [4].

However, little has been reported on the analytic solution of polydisperse models, such as free energy. In this paper, we consider two types of models of polydisperse systems with Kac interaction:

(i) Polydisperse lattice-gas model which is inspired by Sollich et al. [5], where a similar model in grand canonical ensemble was considered.
(ii) Continuous polydisperse system.

We consider these models in canonical ensemble formalism, and derive analytic expressions for free energies. Our method of analysis is based on the method of Lebowitz and Penrose [6], where a monodisperse system was considered.

The outline of the paper is as follows. In Sect. 2 we introduce a polydisperse lattice-gas model and obtain the free energy. In Sect. 3 we exhibit phase diagrams for the bidisperse

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model of Sect. 2. In Sect. 4 we briefly describe a polydisperse continuous system. Finally, we present our conclusions in Sect. 5.

Note Added After having submitted the first manuscript of the present paper, the author has been informed of Ref. [7], where similar results had been obtained for continuous systems. One of the points of the present paper is the analysis of a lattice-gas model, for which everything can be written down explicitly.

2 Polydisperse Lattice-Gas Model (PLGM)

In this section, we define a polydisperse lattice-gas model and obtain a rigorous expression for the free energy. The basic idea is derived from Lebowitz and Penrose [6], where a monodisperse system is considered. We compute an upper bound for the free energy in Sect. 2.2 and a lower bound in Sect. 2.3. Then we show the two agree. From now on, we abbreviate the polydisperse lattice-gas model as PLGM.

2.1 Definitions and Assumptions

We first define the model we consider. We consider a ν-dimensional hypercubic lattice $\Omega = \{(x_1, x_2, \ldots, x_\nu) | x_i \in \mathbb{Z}, 0 \le x_i \le L\}$ with periodic boundary conditions, where L is a large integer. Let $|\Omega|$ be the volume of Ω. We consider n types of particles whose numbers are fixed. Let N^j be the number of particles of type j $(j = 1, 2, \ldots, n)$ and let $N = \sum_{j=1}^{n} N^j$ be the total number of particles. Each lattice point $x \in \Omega$ can be occupied by at most one particle. We write $\beta \equiv 1/kT$ (k is the Boltzmann constant and T is the temperature).

Let $d_1, d_2, \ldots, d_n$ be positive constants. The particle configuration on Ω can be expressed by $\{D_x\}_{x\in\Omega}$, where $D_x = 0, d_1, d_2, \ldots, d_n$ denotes the type of particle at x ($D_x = d_j$ means there is a particle of type j at x, and $D_x = 0$ indicates that there is no particle at x). The *Hamiltonian* of the system is given by

$$\mathcal{H} \equiv \sum_{\substack{x<y \\ x,y\in\Omega}} w(x-y, \gamma) D_x D_y, \tag{2.1}$$

where $w(x-y, \gamma)$ denotes the Kac interaction potential (explained later) between particles at x and y. Note that the interaction energy between particles depends on types of particles, due to $D_x D_y$ in the interaction. We define the *partition function* $Z(\vec{N}, |\Omega|, \gamma)$ for given $N^1, N^2, \ldots, N^n$ as

$$Z(\vec{N}, |\Omega|, \gamma) \equiv \left(\prod_{x\in\Omega} \sum_{D_x = 0, d_1, d_2, \ldots, d_n} \right) e^{-\beta\mathcal{H}} \left(\prod_{j=1}^{n} I\left[\sum_{x\in\Omega} I\left[D_x = d_j\right] = N^j \right] \right), \tag{2.2}$$

where $\vec{N} \equiv (N^1, N^2, \ldots, N^n)$. In the above, $I[E]$ is the *indicator function* for the event E given by

$$I[E] = \begin{cases} 1 & (E \text{ is satisfied}), \\ 0 & (\text{otherwise}). \end{cases} \tag{2.3}$$

The *free energy* $A(\vec{N}, |\Omega|, \gamma)$ is defined by

$$A(\vec{N}, |\Omega|, \gamma) \equiv -\beta^{-1} \log Z(\vec{N}, |\Omega|, \gamma). \tag{2.4}$$

We are interested in the infinite volume limit of the *free energy density* $a(\vec{\rho}, \gamma)$ defined by

$$a(\vec{\rho}, \gamma) \equiv \lim_{|\Omega| \to \infty} A(\vec{N}, |\Omega|, \gamma)/|\Omega|, \tag{2.5}$$

where $\vec{\rho} \equiv (\rho^1, \rho^2, \ldots, \rho^n)$ with $\rho^j = \frac{N^j}{|\Omega|}$. In the above we fix ρ^j $(j = 1, 2, \ldots, n)$ and let $|\Omega| \to \infty$. The total density of particles is $\rho = \sum_{j=1}^{n} \rho^j$.

We now specify the interaction potential considered in this paper. $w(x, \gamma)$ is the Kac potential which is given by

$$w(x, \gamma) = \gamma^{\nu} \varphi(\gamma x), \tag{2.6}$$

where γ is a positive parameter, which specifies the range of the potential (the range of the Kac potential is proportional to the reciprocal of γ).

We impose the following conditions on $\varphi(x)$:

$$\text{(a)} \quad \varphi(x) \le 0 \quad \text{for all } x, \quad \text{i.e.} \quad w(x, \gamma) \le 0 \quad \text{for all } x, \tag{2.7}$$

$$\text{(b)} \quad |\varphi(x)| < D_3 |x|^{-\nu-\epsilon} \quad \text{for all } x, \tag{2.8}$$

$$\text{(c)} \quad \varphi(x) \quad \text{is continuous at } x = 0, \tag{2.9}$$

$$\text{(d)} \quad \int \varphi(x) dx \quad \text{exists as a Riemann integral,} \tag{2.10}$$

where D_3 and ϵ are positive constants.

Note that $w(x, \gamma)$ has the following property:

$$\lim_{\gamma \to 0} w(x, \gamma) = 0 \quad \text{for all } x. \tag{2.11}$$

We introduce

$$\int w(x, \gamma) dx = \int \varphi(x) dx \equiv \alpha, \tag{2.12}$$

which is independent of γ.

2.2 Upper Bound on the Free Energy in PLGM

In this section, we derive an upper bound on the free energy. As depicted in Fig. 1, we divide the cube Ω into M smaller cubical regions $\omega_1, \omega_2, \ldots, \omega_M$, whose linear size is $(s + t)$, which is a submultiple of the side of Ω. Thus, the system volume $|\Omega|$ is given by

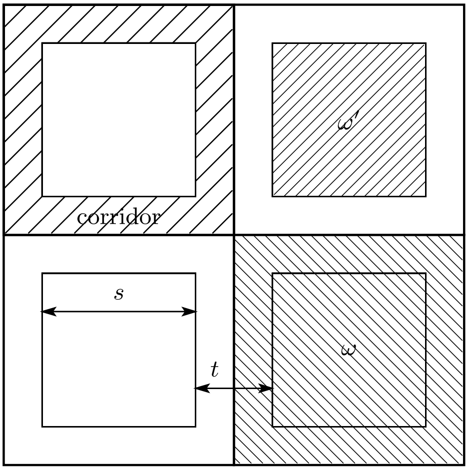
$$|\Omega| = M(s + t)^{\nu}. \tag{2.13}$$

Also let ω_i' $(i = 1, 2, \ldots, M)$ be the cube of side s consisting of all points within ω_i whose distance from the boundary of ω_i is at least $\frac{1}{2}t$. We call ω_i or ω_i' the *cell*.

Let N_i be the number of particles in ω_i' $(i = 1, 2, \ldots, M)$ and let N_i^j be the number of the j^{th} $(j = 1, 2, \ldots, n)$ particle in ω_i'. These satisfy $N_1 + N_2 + \cdots + N_M = N$ and $N_i^1 + N_i^2 + \cdots + N_i^n = N_i$.

We define $\tilde{Z}(\{N_i\}, \{p_i^j\})$ as the contribution to (2.2) from configurations with fixed N_i and with fixed p_i^j, where $p_i^j = N_i^j / N_i$ $(i = 1, 2, \ldots, M$ and $j = 1, 2, \ldots, n)$ is the ratio of the j^{th} particle in ω_i'; $\sum_{j=1}^{n} p_i^j = 1$. $\tilde{Z}(\{N_i\}, \{p_i^j\})$ is given by

Fig. 1 Division of Ω into cells



$$\tilde{Z}(\{N_i\},\{p_i^j\}) = \left\{\prod_{i=1}^{M}\left(\prod_{x\in\omega_i'}\sum_{D_x=0,d_1,d_2,\ldots,d_n}\right)\right\}\exp\left\{-\beta\sum_{\substack{x<y\\ x\in\omega_i',y\in\omega_j'\\ i\le j\le M}} w(x-y,\gamma)D_xD_y\right\}$$
$$\times\left\{\prod_{i=1}^{M}\left(\prod_{j=1}^{n} I\left[\sum_{x\in\omega_i'} I\left[D_x=d_j\right]=N_ip_i^j\right]\right)\right\}. \qquad (2.14)$$

To count the number of terms in the sum of $\tilde{Z}(\{N_i\},\{p_i^j\})$, we have to consider the combination number of particle positions. The number of ways to choose N_i particle positions in ω_i' is $\binom{|\omega_i'|}{N_i}=\binom{s^\nu}{N_i}$. Moreover, the number of ways to choose n types of particles from N_i particle positions is given by the multinomial coefficient

$$\binom{N_i}{p_i^1N_i,\,p_i^2N_i,\ldots,p_i^nN_i}$$
$$=\binom{N_i}{p_i^1N_i}\binom{N_i-p_i^1N_i}{p_i^2N_i}\binom{N_i-(p_i^1+p_i^2)N_i}{p_i^3N_i}\cdots\binom{N_i-(p_i^1+p_i^2+\cdots+p_i^{n-2})N_i}{p_i^{n-1}N_i}.$$

Therefore, the combination number of particle positions in ω_i' is $\binom{s^\nu}{N_i}\binom{N_i}{p_i^1N_i,p_i^2N_i,\ldots,p_i^nN_i}$.

Based on the above consideration, we get the following lower bound.

$$\tilde{Z}(\{N_i\},\{p_i^j\}) \ge \left\{\prod_{i=1}^{M}\binom{s^\nu}{N_i}\binom{N_i}{p_i^1N_i,\,p_i^2N_i,\ldots,p_i^nN_i}\right\}$$
$$\times\exp\left\{-\beta\sum_{i<j\le M}N_iN_j\left(\sum_{k=1}^{n}p_i^kd_k\right)\left(\sum_{k=1}^{n}p_j^kd_k\right)w_{\max}(\mathbf{k}_{ij},\gamma)\right.$$
$$\left.-\beta\sum_{i=1}^{M}\binom{N_i}{2}\left(\sum_{j=1}^{n}p_i^jd_j\right)^2 w_{\max}(\mathbf{k}_{ii},\gamma)\right\}, \qquad (2.15)$$

where

$$w_{\max}(\mathbf{k}_{ij},\gamma) \equiv \max_{x\in\omega_i, y\in\omega_j} w(x-y,\gamma) = \max_{\mathbf{r}\in\omega_o} w(\mathbf{k}_{ij}+2\mathbf{r},\gamma). \tag{2.16}$$

In the above, ω_o is a ν-dimensional hypercube of side $(s+t)$ centered at the origin, and $\mathbf{k}_{ij}$ is the vector from the center of ω_i to that of ω_j.

Since $Z(\vec{N},|\Omega|,\gamma) \geq \tilde{Z}(\{N_i\},\{p_i^j\})$, we obtain the following upper bound from (2.15).

$$\begin{aligned} A(\vec{N},|\Omega|,\gamma) \leq & -\beta^{-1}\log\left\{\prod_{i=1}^{M}\frac{(s^\nu)!}{(s^\nu-N_i)!(p_i^1N_i)!(p_i^2N_i)!\cdots(p_i^nN_i)!}\right\} \\ & + \sum_{i<j\leq M} N_iN_j\left(\sum_{k=1}^n p_i^k d_k\right)\left(\sum_{k=1}^n p_j^k d_k\right) w_{\max}(\mathbf{k}_{ij},\gamma) \\ & + \frac{1}{2}\sum_{i=1}^M N_i(N_i-1)\left(\sum_{j=1}^n p_i^j d_j\right)^2 w_{\max}(\mathbf{k}_{ii},\gamma) \end{aligned} \tag{2.17}$$

Because the above inequality holds for any choice of N_i and p_i^j ($i=1,2,\ldots,M$ and $j=1,2,\ldots,n$), we consider the special case of $N_1=N_2=\cdots=N_M=\rho(s+t)^\nu$ and $p_i^j=p^j$; then, we get

$$\begin{aligned} & A(\vec{N},|\Omega|,\gamma)/|\Omega| \\ & \quad \leq -\beta^{-1}(s+t)^{-\nu}\log\left\{\frac{(s^\nu)!}{(s^\nu-\rho(s+t)^\nu)!(p^1\rho(s+t)^\nu)!(p^2\rho(s+t)^\nu)!\cdots(p^n\rho(s+t)^\nu)!}\right\} \\ & \quad + \frac{1}{2}\rho^2\left(\sum_{j=1}^n p^j d_j\right)^2 \frac{(s+t)^\nu}{M}\sum_{i=1}^M{\sum_{j=1}^M}' w_{\max}(\mathbf{k}_{ij},\gamma) \\ & \quad + \frac{1}{2}\rho\left\{\rho(s+t)^\nu-1\right\}\left(\sum_{j=1}^n p^j d_j\right)^2 \frac{1}{M}\sum_{i=1}^M w_{\max}(\mathbf{k}_{ii},\gamma), \end{aligned} \tag{2.18}$$

where ${\sum_{j=1}^M}'$ means a sum with the $j=i$ term omitted.

We take the triple limit $|\Omega|\to\infty$, $\gamma\to 0$, $s\to\infty$, in this order, where the final limit $(s\to\infty)$ is taken in such a way that

$$t/s\to 0 \quad \text{and} \quad s^\nu/t^{\nu+\epsilon}\to 0 \quad \text{as } s\to\infty. \tag{2.19}$$

For the second term on the right hand side in (2.18), we obtain

$$\begin{aligned} \frac{(s+t)^\nu}{M}\sum_{i=1}^M{\sum_{j=1}^M}' w_{\max}(\mathbf{k}_{ij},\gamma) & \to (s+t)^\nu{\sum_{\mathbf{k}}}' w_{\max}(\mathbf{k},\gamma) \quad (\text{as } |\Omega|\to\infty) \\ & \to \alpha \quad (\text{as } \gamma\to 0). \end{aligned} \tag{2.20}$$

The first line of (2.20) is obtained, because (see (2.14) in [6]):

$$\lim_{|\Omega|\to\infty}\frac{1}{M}\sum_{i=1}^M{\sum_{j=1}^M}' w_{\max}(\mathbf{k}_{ij},\gamma) = {\sum_{\mathbf{k}}}' w_{\max}(\mathbf{k},\gamma), \tag{2.21}$$

where $\sum_{\mathbf{k}}{}'$ is an infinite sum over the complete infinite lattice of possible vectors $\mathbf{k}_{ij}$ except $\mathbf{k}=0$.

Also, the second line of (2.20) is obtained as follows. By (2.6) and (2.16), we write

$$(s+t)^{\nu}\sum_{\mathbf{k}}{}' w_{\max}(\mathbf{k},\gamma)=2^{-\nu}\sum_{\mathbf{n}}{}'\Delta\max_{x\in\Delta_{\mathbf{n}}}\varphi(x), \tag{2.22}$$

where $\Delta_{\mathbf{n}}$ stands for the ν-dimensional hypercube of side $2\gamma(s+t)$ centered at the point $\gamma(s+t)\mathbf{n}$ with its sides parallel to those of Ω, and $\Delta\equiv 2^{\nu}\gamma^{\nu}(s+t)^{\nu}$ is the volume of one of the cubes $\Delta_{\mathbf{n}}$. Now, take the $\gamma\to 0$ limit to obtain

$$(s+t)^{\nu}\lim_{\gamma\to 0}\sum_{\mathbf{k}}{}' w_{\max}(\mathbf{k},\gamma)=\int\varphi(x)dx\equiv\alpha. \tag{2.23}$$

For the third term on the right hand side in (2.18), using (2.11), we obtain

$$\lim_{\gamma\to 0}\lim_{|\Omega|\to\infty}\frac{1}{M}\sum_{i=1}^{M}w_{\max}(\mathbf{k}_{ii},\gamma)=0. \tag{2.24}$$

We now write $a(\vec{\rho},0+)\equiv\lim_{\gamma\to 0}a(\vec{\rho},\gamma)$. Taking the triple limit ($|\Omega|\to\infty$, $\gamma\to 0$, $s\to\infty$, in this order) of (2.18) with the help of (2.20) and (2.24), we obtain

$$a(\vec{\rho},0+)\le\beta^{-1}\left\{\rho\log\rho+(1-\rho)\log(1-\rho)+\rho\sum_{j=1}^{n}p^{j}\log p^{j}+\frac{1}{2}\beta\rho^{2}\alpha\left(\sum_{j=1}^{n}p^{j}d_{j}\right)^{2}\right\}, \tag{2.25}$$

where we have used the Stirling's formula for the first term on the right hand side in (2.18).

Substituting $p^{1}=\rho^{1}/\rho$, $p^{2}=\rho^{2}/\rho,\ldots,p^{n}=\rho^{n}/\rho$ into (2.25), we obtain

$$a(\vec{\rho},0+)\le\beta^{-1}\left\{(1-\rho)\log(1-\rho)+\sum_{j=1}^{n}\rho^{j}\log\rho^{j}+\frac{1}{2}\beta\alpha\left(\sum_{j=1}^{n}\rho^{j}d_{j}\right)^{2}\right\}. \tag{2.26}$$

(2.26) can be improved by using the fact that $a(\vec{\rho},\gamma)$ is a convex function, and in particular, $a(\vec{\rho},0+)$ is a convex function. This leads to

$$a(\vec{\rho},0+)\le\beta^{-1}\mathrm{CE}\left\{(1-\rho)\log(1-\rho)+\sum_{j=1}^{n}\rho^{j}\log\rho^{j}+\frac{1}{2}\beta\alpha\left(\sum_{j=1}^{n}\rho^{j}d_{j}\right)^{2}\right\}, \tag{2.27}$$

where for any function $f(\vec{\rho})$, $\mathrm{CE}\{f(\vec{\rho})\}$ means the *convex envelope* of the function, defined as $\mathrm{CE}\{f(\vec{\rho})\}\equiv\sup\phi(\vec{\rho})$, where sup is taken over all $\phi(\vec{\rho})$ with the following properties:

$$\phi(\vec{\rho})\quad\text{is convex,} \tag{2.28}$$

$$\phi(\vec{\rho})\le f(\vec{\rho})\quad\text{for all }\vec{\rho}. \tag{2.29}$$

(2.27) is the desired upper bound on the free energy.

2.3 Lower Bound on the Free Energy in PLGM

Analogous to Sect. 2.2, let $Z(\{N_i\},\{p_i^j\})$ be the contribution to (2.2) from configurations with N_i particles in the cell ω_i and with fixed ratio p_i^j ($i=1,2,\ldots,M,\ j=1,2,\ldots,n$ and $N_1+N_2+\cdots+N_M=N$). Then, we have

$$Z(\vec{N},|\Omega|,\gamma)=\sum_{N_1,\ldots,N_M}\ \sum_{\{p_i^1,\ldots,p_i^n\}} Z(\{N_i\},\{p_i^j\}), \tag{2.30}$$

where $\sum_{N_1,\ldots,N_M}$ is the sum over all sets of M nonnegative integers adding up to N and $\sum_{\{p_i^1,\ldots,p_i^n\}}$ is the sum over all possible p_i^j which satisfy $\sum_{i=1}^n N_i p_i^j \equiv N^j$.

We consider the number of terms in the sum of (2.30). There are $(N+M-1)!/N!(M-1)!$ $(=\binom{N+M-1}{N})$ terms in the sum $\sum_{N_1,\ldots,N_M}$. The number of all possible values of p_i^j is equal to the number of terms in the sum $\sum_{\{p_i^1,\ldots,p_i^n\}}$. Let N_i^j be the number of j^{th} particle in ω_i. First, $p_i^1=N_i^1/N_i$ and possible values of N_i^1 are $N_i^1=0,1,\ldots,N_i$. Thus, the number of all possible values of p_i^1 is N_i+1. Secondly, $p_i^2=N_i^2/N_i$ and possible values of N_i^2 are $N_i^2=0,1,\ldots,N_i-p_i^1N_i$. Therefore, the number of all possible values of p_i^2 is $N_i-p_i^1N_i+1$. With a similar argument for $p_i^3,p_i^4,\ldots,p_i^{n-1}$, the number of all possible values of p_i^j in ω_i is $(N_i+1)(N_i-p_i^1N_i+1)(N_i-(p_i^1+p_i^2)N_i+1)\cdots(N_i-(p_i^1+p_i^2+\cdots+p_i^{n-2})N_i+1)$. From the above consideration, we conclude that the number of terms in the sum $\sum_{\{p_i^1,\ldots,p_i^n\}}$ is $\prod_{i=1}^M (N_i+1)(N_i-p_i^1N_i+1)(N_i-(p_i^1+p_i^2)N_i+1)\cdots(N_i-(p_i^1+p_i^2+\cdots+p_i^{n-2})N_i+1)$.

Therefore, we have the following upper bound from (2.30).

$$\begin{aligned} Z(\vec{N},|\Omega|,\gamma) &\le \frac{(N+M-1)!}{N!(M-1)!} \\ &\quad\times \max_{\{N_i\},\{p_i^j\}}\Bigg[\Bigg\{\prod_{i=1}^M (N_i+1)(N_i-p_i^1N_i+1)(N_i-(p_i^1+p_i^2)N_i+1)\cdots \\ &\quad\times(N_i-(p_i^1+p_i^2+\cdots+p_i^{n-2})N_i+1)\Bigg\}Z(\{N_i\},\{p_i^j\})\Bigg], \end{aligned} \tag{2.31}$$

where $\max_{\{N_i\},\{p_i^j\}}$ is taken over all possible combinations of N_i, p_i^j.

For $Z(\{N_i\},\{p_i^j\})$, we get the following inequality analogous to (2.15).

$$\begin{aligned} Z(\{N_i\},\{p_i^j\}) &\le \left\{\prod_{i=1}^M \binom{(s+t)^\nu}{N_i}\binom{N_i}{p_i^1N_i,\,p_i^2N_i,\ldots,p_i^nN_i}\right\} \\ &\quad\times\exp\left\{-\beta\sum_{i\le j\le M}N_iN_j\left(\sum_{k=1}^n p_i^k d_k\right)\left(\sum_{k=1}^n p_j^k d_k\right)w_{\min}(\mathbf{k}_{ij},\gamma)\right\}, \end{aligned} \tag{2.32}$$

where

$$w_{\min}(\mathbf{k}_{ij},\gamma)\equiv \min_{x\in\omega_i,y\in\omega_j} w(x-y,\gamma)=\min_{\mathbf{r}\in\omega_o} w(\mathbf{k}_{ij}+2\mathbf{r},\gamma). \tag{2.33}$$

Since

$$N_i\left(\sum_{k=1}^{n} p_i^k d_k\right)\cdot N_j\left(\sum_{k=1}^{n} p_j^k d_k\right) \le \frac{1}{2}{N_i}^2\left(\sum_{k=1}^{n} p_i^k d_k\right)^2 + \frac{1}{2}{N_j}^2\left(\sum_{k=1}^{n} p_j^k d_k\right)^2,$$

and $w_{\min}(\mathbf{k}_{ij}, \gamma) \le 0$ by (2.7), we obtain

$$\begin{aligned} &-\sum_{i\le j\le M} N_i N_j\left(\sum_{k=1}^{n} p_i^k d_k\right)\left(\sum_{k=1}^{n} p_j^k d_k\right) w_{\min}(\mathbf{k}_{ij}, \gamma) \\ &\quad\le -\frac{1}{2}\sum_{i=1}^{M} {N_i}^2\left(\sum_{k=1}^{n} p_i^k d_k\right)^2 \sum_{j=1}^{M} w_{\min}(\mathbf{k}_{ij}, \gamma). \end{aligned} \tag{2.34}$$

Extending the sum over j in (2.34) to infinity, we have

$$\sum_{j=1}^{M} w_{\min}(\mathbf{k}_{ij}, \gamma) \ge \sum_{\mathbf{k}} w_{\min}(\mathbf{k}, \gamma). \tag{2.35}$$

From (2.31), (2.32), (2.34), and (2.35), we obtain

$$\begin{aligned} &A(\vec{N}, |\Omega|, \gamma)/|\Omega| \\ &\quad\ge \beta^{-1}|\Omega|^{-1}\log\left\{\frac{N!(M-1)!}{(N+M-1)!}\right\} \\ &\qquad+ |\Omega|^{-1}\min_{\{N_i\},\{p_i^j\}}\sum_{i=1}^{M}\Bigg[-\beta^{-1}\log\Bigg\{(N_i+1)(N_i - p_i^1 N_i + 1) \\ &\qquad\times (N_i - (p_i^1 + p_i^2)N_i + 1)\cdots(N_i - (p_i^1 + p_i^2 + \cdots + p_i^{n-2})N_i + 1) \\ &\qquad\times \binom{(s+t)^\nu}{N_i}\binom{N_i}{p_i^1 N_i, p_i^2 N_i, \ldots, p_i^n N_i}\Bigg\} \\ &\qquad+ \frac{1}{2}{N_i}^2\left(\sum_{j=1}^{n} p_i^j d_j\right)^2 \sum_{\mathbf{k}} w_{\min}(\mathbf{k}, \gamma)\Bigg]. \end{aligned} \tag{2.36}$$

The following inequality holds for any function $F(\cdot)$.

$$\begin{aligned} &M^{-1}\sum_{i=1}^{M} F(N_i, p_i^1 N_i, p_i^2 N_i, \ldots, p_i^n N_i) \\ &\ge M^{-1}\sum_{i=1}^{M}\mathrm{CE}\left\{F(N_i, p_i^1 N_i, p_i^2 N_i, \ldots, p_i^n N_i)\right\} \\ &\ge \mathrm{CE}\left\{F\left(M^{-1}\sum_{i=1}^{M} N_i, M^{-1}\sum_{i=1}^{M} p_i^1 N_i, M^{-1}\sum_{i=1}^{M} p_i^2 N_i, \ldots, M^{-1}\sum_{i=1}^{M} p_i^n N_i\right)\right\} \\ &= \mathrm{CE}\left\{F(M^{-1}\rho|\Omega|, M^{-1}\rho^1|\Omega|, M^{-1}\rho^2|\Omega|, \ldots, M^{-1}\rho^n|\Omega|)\right\} \\ &= \mathrm{CE}\left\{F(\rho(s+t)^\nu, \rho^1(s+t)^\nu, \rho^2(s+t)^\nu, \ldots, \rho^n(s+t)^\nu)\right\}, \end{aligned} \tag{2.37}$$

where the second line follows from the fact that $\mathrm{CE}\{F(\cdot)\}$ is a lower bound on $F(\cdot)$, and the third from the fact that $\mathrm{CE}\{F(\cdot)\}$ is convex.

Using (2.37) in the second term of (2.36), we obtain

$$
\begin{aligned}
&|\Omega|^{-1} \min_{\{N_i\},\{p_i^j\}} \sum_{i=1}^{M} \Bigg[-\beta^{-1} \log \Bigg\{ (N_i+1)(N_i - p_i^1 N_i + 1) \\
&\quad \times (N_i - (p_i^1 + p_i^2)N_i + 1) \cdots (N_i - (p_i^1 + p_i^2 + \cdots + p_i^{n-2})N_i + 1) \\
&\quad \times \binom{(s+t)^\nu}{N_i} \binom{N_i}{p_i^1 N_i, p_i^2 N_i, \ldots, p_i^n N_i} \Bigg\} \\
&\quad + \frac{1}{2} N_i{}^2 \Bigg(\sum_{j=1}^{n} p_i^j d_j \Bigg)^2 \sum_{\mathbf{k}} w_{\min}(\mathbf{k}, \gamma) \Bigg] \\
&\geq \beta^{-1}(s+t)^{-\nu} \mathrm{CE} \Bigg[-\log \Bigg\{ (\rho(s+t)^\nu + 1)((\rho - \rho^1)(s+t)^\nu + 1) \cdots \\
&\quad \times ((\rho - \rho^1 - \rho^2 - \cdots - \rho^{n-1})(s+t)^\nu + 1) \\
&\quad \times \binom{(s+t)^\nu}{\rho(s+t)^\nu} \binom{\rho(s+t)^\nu}{\rho^1(s+t)^\nu, \rho^2(s+t)^\nu, \ldots, \rho^n(s+t)^\nu} \Bigg\} \\
&\quad + \frac{1}{2} \beta \Bigg(\sum_{j=1}^{n} \rho^j d_j \Bigg)^2 (s+t)^{2\nu} \sum_{\mathbf{k}} w_{\min}(\mathbf{k}, \gamma) \Bigg] \\
&\approx \beta^{-1}(s+t)^{-\nu} \mathrm{CE} \Bigg\{ -\log(\rho(s+t)^\nu + 1) - \log((\rho - \rho^1)(s+t)^\nu + 1) - \cdots \\
&\quad - \log((\rho - \rho^1 - \cdots - \rho^{n-1})(s+t)^\nu + 1) + (s+t)^\nu \log(1-\rho) + \frac{1}{2} \log(1-\rho) \\
&\quad - \rho(s+t)^\nu \log \frac{1-\rho}{\rho^n} + \frac{n}{2} \log 2\pi (s+t)^\nu + \frac{1}{2} \log \rho^1 \rho^2 \cdots \rho^n \\
&\quad + (s+t)^\nu \sum_{j=1}^{n-1} \rho^j \log \frac{\rho^j}{\rho^n} + \frac{1}{2} \beta \Bigg(\sum_{j=1}^{n} \rho^j d_j \Bigg)^2 (s+t)^{2\nu} \sum_{\mathbf{k}} w_{\min}(\mathbf{k}, \gamma) \Bigg\},
\end{aligned} \tag{2.38}
$$

where we have used the Stirling's formula for the rightmost term of (2.38).

For the first term of (2.36), we get

$$
\begin{aligned}
&\lim_{s\to\infty} \lim_{\gamma\to 0} \lim_{|\Omega|\to\infty} \beta^{-1} |\Omega|^{-1} \log \left\{ \frac{N!(M-1)!}{(N+M-1)!} \right\} \\
&\quad = \lim_{s\to\infty} \lim_{\gamma\to 0} \beta^{-1} \left[-(s+t)^{-\nu} \log\{1 + \rho(s+t)^\nu\} - \rho \log\{1 + \rho^{-1}(s+t)^{-\nu}\} \right] \\
&\quad = 0,
\end{aligned} \tag{2.39}
$$

where we have also used the Stirling's formula.

Analogous to (2.23), we obtain

$$(s+t)^{\nu}\lim_{\gamma\to 0}\sum_{\mathbf{k}} w_{\min}(\mathbf{k},\gamma)=\int\varphi(x)dx\equiv\alpha. \tag{2.40}$$

Also, we employ the following lemma (see (4.23) in [6]): let $f_n(\xi)$ be a sequence of functions converging uniformly on a set to $f(\xi)$ as $n\to\infty$. Then, we have

$$\lim_{n\to\infty}\mathrm{CE}\{f_n(\xi)\}=\mathrm{CE}\{f(\xi)\}. \tag{2.41}$$

Substituting (2.38) into (2.36), we take the triple limit ($|\Omega|\to\infty$, $\gamma\to 0$, $s\to\infty$) to obtain the following inequality with the help of (2.39), (2.40), and (2.41).

$$\begin{aligned} a(\vec{\rho},0+)&\geq\beta^{-1}\mathrm{CE}\left\{\log(1-\rho)-\rho\log\frac{1-\rho}{\rho^n}+\sum_{j=1}^{n-1}\rho^j\log\frac{\rho^j}{\rho^n}+\frac{1}{2}\beta\left(\sum_{j=1}^{n}\rho^j d_j\right)^2\alpha\right\}\\ &=\beta^{-1}\mathrm{CE}\left\{(1-\rho)\log(1-\rho)+\sum_{j=1}^{n}\rho^j\log\rho^j+\frac{1}{2}\beta\alpha\left(\sum_{j=1}^{n}\rho^j d_j\right)^2\right\}. \end{aligned} \tag{2.42}$$

(2.42) is the desired lower bound on the free energy. The lower bound (2.42) and the upper bound (2.27) are equal. Therefore we conclude

$$a(\vec{\rho},0+)=\beta^{-1}\mathrm{CE}\left\{\tilde{a}^0(\vec{\rho})+\frac{1}{2}\beta\alpha\left(\sum_{j=1}^{n}\rho^j d_j\right)^2\right\}, \tag{2.43}$$

where $\tilde{a}^0(\vec{\rho})\equiv(1-\rho)\log(1-\rho)+\sum_{j=1}^{n}\rho^j\log\rho^j$ represents lattice-gas hard core repulsions.

3 Phase Diagram in PLGM

In this section, we obtain phase diagrams for the free energy derived in Sect. 2. We restrict ourselves to a bidisperse case, whose phase diagram can be drawn in three dimensions.

In the bidisperse case, we obtain the following equation from (2.43).

$$a(\vec{\rho},0+)=\beta^{-1}\mathrm{CE}\left\{f(\rho^1,\rho^2)\right\}, \tag{3.1}$$

where

$$f(x,y)\equiv(1-x-y)\log(1-x-y)+x\log x+y\log y+\frac{1}{2}\beta\alpha(ax+by)^2, \tag{3.2}$$

with $a=d_1$ and $b=d_2$.

The phase diagram for (3.1) is composed of three domains—a liquid phase, a gas phase, and a coexisting phase. In the liquid or gas phase, the quantity in the braces in (3.1) is itself convex. Therefore, we get

$$a(\vec{\rho},0+)=\beta^{-1}f(\rho^1,\rho^2). \tag{3.3}$$

On the other hand, the quantity in the braces in (3.1) is not convex in the coexisting phase, and the free energy is expressed as a linear combination of free energies at two points on the boundary. In the following we explain in detail how to determine the boundary and the free energy in the coexisting phase.

Let $(x', y', f(x', y'))$ be a point in the coexisting phase and $(x_1, y_1, f(x_1, y_1))$, $(x_2, y_2, f(x_2, y_2))$ be the corresponding two points on the boundary. Then $(x', y', f(x', y'))$, $(x_1, y_1, f(x_1, y_1))$, and $(x_2, y_2, f(x_2, y_2))$ must lie on a line segment. Furthermore, the tangent plane at $(x_1, y_1, f(x_1, y_1))$ must coincide with that at $(x_2, y_2, f(x_2, y_2))$.

The equation of the tangent plane at $(x_1, y_1, f(x_1, y_1))$ is given by

$$z - f(x_1, y_1) = f_x(x_1, y_1)(x - x_1) + f_y(x_1, y_1)(y - y_1). \tag{3.4}$$

Analogously, the equation of the tangent plane at $(x_2, y_2, f(x_2, y_2))$ is given by

$$z - f(x_2, y_2) = f_x(x_2, y_2)(x - x_2) + f_y(x_2, y_2)(y - y_2). \tag{3.5}$$

Therefore, we obtain the following equations as the condition that (3.4) coincides with (3.5).

$$f_x(x_1, y_1) = f_x(x_2, y_2), \tag{3.6}$$

$$f_y(x_1, y_1) = f_y(x_2, y_2), \tag{3.7}$$

$$\begin{aligned} &f(x_1, y_1) - x_1 f_x(x_1, y_1) - y_1 f_y(x_1, y_1) \\ &\quad = f(x_2, y_2) - x_2 f_x(x_2, y_2) - y_2 f_y(x_2, y_2). \end{aligned} \tag{3.8}$$

Three points (x', y'), (x_1, y_1), (x_2, y_2) are on the same line segment if there exists $0 \le t \le 1$ such that

$$t \begin{pmatrix} x_1 \\ y_1 \end{pmatrix} + (1 - t) \begin{pmatrix} x_2 \\ y_2 \end{pmatrix} = \begin{pmatrix} x' \\ y' \end{pmatrix}. \tag{3.9}$$

By explicit calculations, (3.6), (3.7), and (3.8) yield

$$\begin{aligned} &-\log(1 - x_1 - y_1) + \log x_1 + \beta\alpha a(ax_1 + by_1) \\ &\quad = -\log(1 - x_2 - y_2) + \log x_2 + \beta\alpha a(ax_2 + by_2), \end{aligned} \tag{3.10}$$

$$\begin{aligned} &-\log(1 - x_1 - y_1) + \log y_1 + \beta\alpha b(ax_1 + by_1) \\ &\quad = -\log(1 - x_2 - y_2) + \log y_2 + \beta\alpha b(ax_2 + by_2), \end{aligned} \tag{3.11}$$

$$\log(1 - x_1 - y_1) - \frac{1}{2}\beta\alpha(ax_1 + by_1)^2 = \log(1 - x_2 - y_2) - \frac{1}{2}\beta\alpha(ax_2 + by_2)^2. \tag{3.12}$$

Solving (3.9), (3.10), (3.11), and (3.12) as simultaneous equations, we can derive two points $(x_1, y_1, f(x_1, y_1))$, $(x_2, y_2, f(x_2, y_2))$ for a given (x', y'), and we obtain the free energy $f(x', y')$ from the following equation.

$$f(x', y') = tf(x_1, y_1) + (1 - t)f(x_2, y_2), \tag{3.13}$$

where t is given by (3.9).

To obtain a phase diagram, we vary (x', y') and find the boundary points $(x_1, y_1, f(x_1, y_1))$, $(x_2, y_2, f(x_2, y_2))$ as above. For $\alpha = -1$, $a = 1$, $b = 2, 3$ and several values of β,

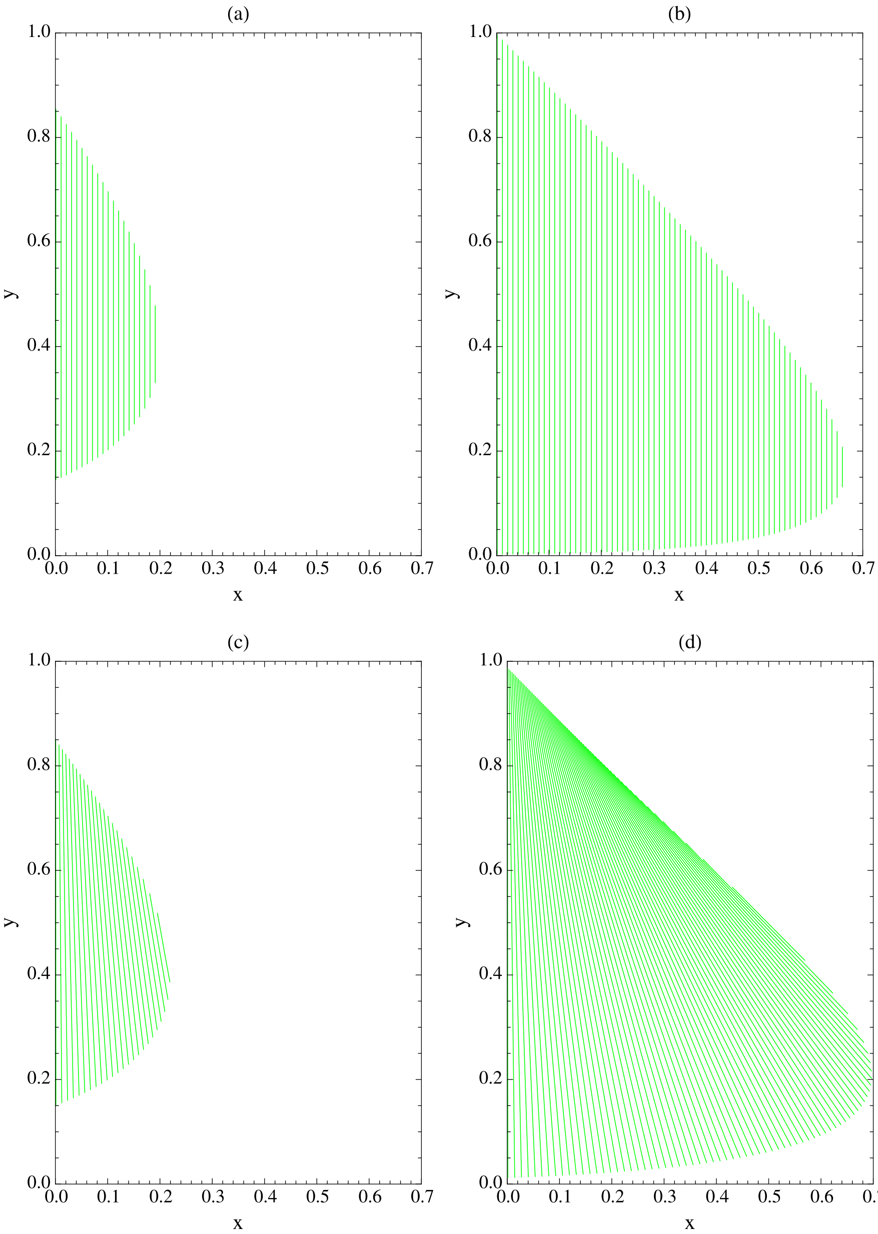


Fig. 2 Phase diagrams at (**a**) $\beta = 1.25, b = 2$, (**b**) $\beta = 3, b = 2$, (**c**) $\beta = 0.55, b = 3$, and (**d**) $\beta = 1, b = 3$ for $\alpha = -1, a = 1$

phase diagrams with the vertical axis x and the transverse y are given in Fig. 2. The domain occupied by line segments indicates the coexisting phase. A set of end points of line segments is the boundary of the coexisting phase.

The above description is about the case where the graph of $f(x, y)$ has a tangent plane at two points. Actually, there are cases where it has a tangent plane at three points. Then,

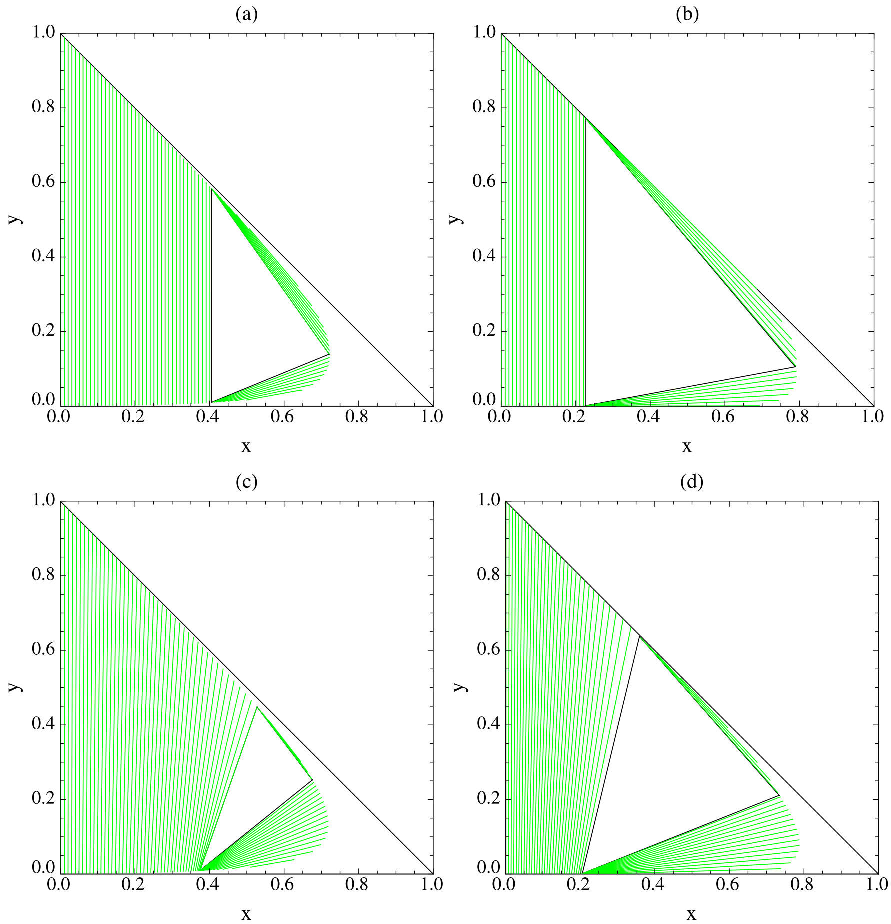


Fig. 3 Phase diagrams at (**a**) $\beta = 3.5, b = 2$, (**b**) $\beta = 4.2, b = 2$, (**c**) $\beta = 3.5, b = 1.98$, and (**d**) $\beta = 4.2, b = 1.95$ for $\alpha = -1, a = 1$

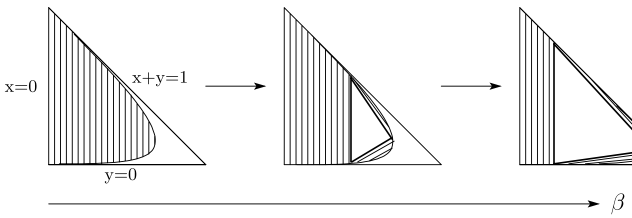


Fig. 4 Schematic phase diagrams for $\alpha = -1, a = 1, b = 2$

the free energy on the triangle region with vertices at three points is expressed as a linear combination of free energies at three points, and we can obtain a phase diagram using the same idea as above. Phase diagrams for $\alpha = -1, a = 1$ and several values of β, b are given in Fig. 3. Schematic phase diagrams are given in Fig. 4, Fig. 5, and Fig. 6 (change of phase diagrams as we increase β is schematically shown in Fig. 4, Fig. 5, and Fig. 6).

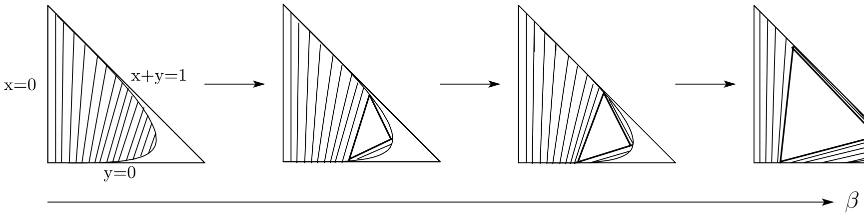


Fig. 5 Schematic phase diagrams for $\alpha = -1, a = 1, b < 2$

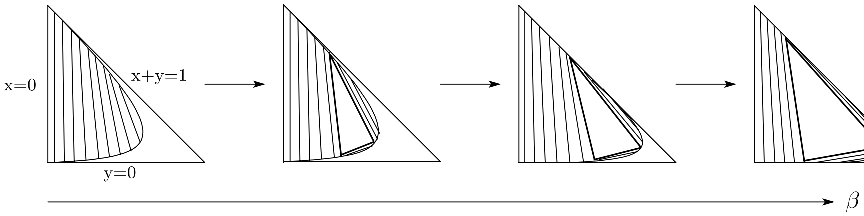


Fig. 6 Schematic phase diagrams for $\alpha = -1, a = 1, b > 2$

We remark that there is a simple scaling relation among β, a, and b. That is, the shape of the coexisting phase for a set (β, a, b) coincides with that for the set $(\beta/C^2, a \times C, b \times C)$, where C is an arbitrary positive constant.

4 Polydisperse Continuous System

In Sect. 2, we have treated a polydisperse discrete system (lattice-gas model). In this section, we briefly introduce a polydisperse continuous system.

Definitions and assumptions are almost the same as Sect. 2.1. We only explain the difference in the following. Let Ω be a ν-dimensional hypercube in $\mathbb{R}^\nu$. We write the potential as $v(x, \gamma)$ $(x \in \mathbb{R}^\nu)$. $v(x, \gamma)$ is given by

$$v(x, \gamma) = q(x) + w(x, \gamma), \tag{4.1}$$

where $q(x)$ is a short-range potential which satisfies

$$q(x) = \infty \quad (|x| < r_0), \tag{4.2}$$

$$|q(x)| < D_2 |x|^{-\nu-\epsilon} \quad (|x| \geq r_0), \tag{4.3}$$

where r_0, D_2, ϵ are positive constants. $w(x, \gamma)$ is the Kac potential as in Sect. 2.1.

There are N particles in Ω, and $x_1, x_2, \ldots, x_N \in \Omega$ indicates each particle's position. Analogous to Sect. 2.1, $D_{x_k} = d_1, d_2, \ldots, d_n$ denotes the type of particle at x_k $(k = 1, 2, \ldots, N)$. The potential energy V of the system is given by

$$V \equiv \sum_{k<l \leq N} D_{x_k} D_{x_l} v(x_k - x_l, \gamma). \tag{4.4}$$

The partition function $Z(\vec{N}, |\Omega|, \gamma)$ is defined by

$$Z(\vec{N}, |\Omega|, \gamma) \equiv \left(\frac{1}{N!}\right)\left(\frac{1}{\beta}\right)^{\frac{\nu N}{2}} \left\{\prod_{k=1}^{N}\left(\sum_{D_{x_k}=d_1,\dots,d_n}\right)\right\} \int_{\Omega}\cdots\int_{\Omega} e^{-\beta V} dx_1 \cdots dx_N. \tag{4.5}$$

Analogous to Sect. 2 and the method of Lebowitz and Penrose [6], we can get the following free energy density.

$$a(\vec{\rho}, +0) = \mathrm{CE}\left\{a^0(\vec{\rho}) + \frac{1}{2}\alpha\left(\sum_{j=1}^{n}\rho^j d_j\right)^2\right\}, \tag{4.6}$$

where $a^0(\vec{\rho})$ is the polydisperse free energy density of the system without the Kac potential, i.e., the system with $v(x,\gamma) = q(x)$. The corresponding quantity for the lattice gas model is $\tilde{a}^0(\vec{\rho})$ of (2.43), which does not depend on the types of particles. We could introduce polydisperse short range interactions for lattice-gas models as well, but if we do so, we cannot write down an explicit form for $\tilde{a}^0(\vec{\rho})$.

5 Conclusion

We have derived rigorous expressions for free energies of polydisperse systems which exhibit liquid-vapor transition. For the bidisperse lattice-gas model, complete phase diagrams have been obtained, which enable us to understand the coexisting phase clearly.

There are some open problems. We have not presented phase diagrams for the polydisperse continuous system, because we do not know the explicit form of the free energy due to the short-range interaction ($a^0(\vec{\rho})$ in (4.6)). It is therefore desirable to investigate $a^0(\vec{\rho})$ in more detail. It is also desirable to consider a polydisperse lattice-gas model with short-range potentials instead of the Kac long-range potential.

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References

1. Sollich, P.: Predicting phase equilibria in polydisperse systems. J. Phys., Condens. Matter **14**, R79 (2002)
2. Banerjee, S., Griffiths, R.B., Widom, M.: Thermodynamic limit for polydisperse fluids. J. Stat. Phys. **104**, 725 (2001)
3. Ioffe, D., Velenik, Y., Zahradnik, M.: Entropy-driven phase transition in a polydisperse hard-rods lattice system. J. Stat. Phys. **122**(4), 761–786 (2006)
4. Kawasaki, T., Araki, T., Tanaka, H.: Correlation between dynamic heterogeneity and medium-range order in two-dimensional glass-forming liquids. Phys. Rev. Lett. **99**, 215701 (2007)
5. Wilding, N.B., Sollich, P., Buzzacchi, M.: Polydisperse lattice-gas model. Phys. Rev. E **77**, 011501 (2008)
6. Lebowitz, J.L., Penrose, O.: Rigorous treatment of the Van Der Waals-Maxwell theory of the liquid-vapor transition. J. Math. Phys. **7**, 98 (1966)
7. Lebowitz, J.L., Hemmer, P.C.: *Systems with Weak Long-Range Potentials*, vol. 5B. Academic Press, New York (1976)