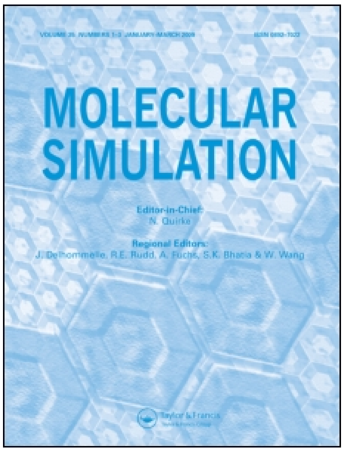

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STUDY OF CLUSTERING IN NONIDEAL ION PLASMA BY A COMBINED OPEN ENSEMBLE MONTE CARLO - CLUSTER EXPANSION METHOD

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The chemical potential and Gibbs free energy of ion clusters are obtained by Monte Carlo method combined with a cluster expansion in a wide range of pressures. Gibbs free energy and configurational energy of the symmetric ion plasma is calculated by Frenkel-Band cluster expansion. The energy is compared with Monte Carlo data for a periodic system.

KEY WORDS: Monte Carlo, cluster, chemical potential, ion plasma.

1 INTRODUCTION

Ion systems of various types have been an object of intensive theoretical and computational study for recent decades. Equilibrium properties and structure of the symmetrical periodic ion system were thoroughly investigated by MC simulation for a wide range of parameters including areas of strong nonideality and in the vicinity of the critical point [1–3]. At gaseous densities far from the condensation region a strong increase in binary and ternary interionic correlations were observed – evidence of ionic clustering [2]. The same clustering phenomena were observed in MC computer experiments of small ion systems enclosed in a spherical box [4, 5]. The formation of clusters is accompanied by peaks in thermal coefficients and anomalies of other properties. In reference [6] the Frenkel and Band (FB) method of physical groups [10] was applied to estimate the equilibrium concentrations of ionic pairs. On the basis of the harmonic approximation structural transitions between open ionic chains and compact clusters were studied [7]. In reference [8] the conditions for stability of a critical nucleus in a computer experiment were formulated.

The data [4, 5] also indicate that screening of the Coulomb potential produces an effective short range interaction. It makes the noninteracting cluster approximation of the FB theory of physical groups [10] a natural tool for the description of strongly nonideal ion plasma. In the noninteracting cluster approximation the free energy of gaseous phase is being expressed as a sum of thermodynamical potentials of clusters. It should be held in mind that alternative approaches based on Mayer group expansion in their initial formulation [9] applied to Coulomb systems produces divergent group integrals, and the renormalisation procedure which accounts for screening results in expressions that are too complicated for numerical use.

In references [11–13] there was suggested and tested on a Lennard-Jones system a method of free energy computation based on the direct calculation of the chemical potential in completely open (μpT) ensembles. In the present paper we apply this method to ion systems.

We intend to calculate chemical potential and Gibbs potential both for small systems and clusters. It is necessary to pay attention to difference in meaning of terms "small system" and "cluster." An N-particle small system enclosed in a sphere of volume V corresponds to a region of $3N$-dimensional configurational space such that $|x_i| \leqslant (3V/4\pi)^{1/3}$, $i = 1 \ldots N$. An n-particle cluster corresponds to a subset of this region (see details in [13]). The cluster expansion over physical groups for an N-particle small system could be constructed in the same way as for a macrosystem. Let our aim be the calculation of the Gibbs free energy of a cluster. This problem is solved by reversion of the cluster expansion: the Gibbs potentials of clusters are being restored from the Gibbs potentials of small systems. The problem of reversion can in principle be solved rigorously since the cluster expansion for a small system contains a finite number of terms. In its turn the Gibbs potential of a small system can be calculated by means of the open ensemble MC method. The Gibbs potential of the macrosystem is then being obtained on the basis of the cluster Gibbs potential data as a sum of low order terms of the physical group expansion for the macrosystem.

2 TWO WAYS OF CALCULATION OF THERMODYNAMICAL POTENTIALS OF THE SMALL SYSTEM

a) With the aid of the open ensemble stationary MC method [13] we calculate chemical potentials of small hard core symmetric ion systems (restricted primitive model – RPM) in a spherical vessel including ion numbers ($n = 1, m = 1$); ($n = 2, m = 1$); ($n = 2, m = 2$) at temperature $T = 0.077$ in a wide range of pressures – $10^{-10} < p < 10^{-1}$ (all data are presented in $k - h - a - q$ – system of units, where k – Boltzmann constant, h – Planck constant, a – core diametre, q – charge of the ion) corresponding to the region of strong nonideality (see the Table). The temperature and pressure range are chosen the same as in [2] to make possible a comparison with results for the periodical system.

The chemical potentials are defined as

$$\begin{aligned} \mu(1, 1) &= G(1, 1) - G(1, 0) \\ \mu(2, 1) &= G(2, 1) - G(1, 1) \\ \mu(2, 2) &= G(2, 2) - G(2, 1) \\ &\ldots\ldots\ldots\ldots \end{aligned} \tag{1}$$

where G is the Gibbs potential.

For the system of n positive and m negative ions with charges $\pm q$ G is determined by NpT – ensemble partition function in a conventional way:

$$G(n, m, p, T) =$$

$$-kT\ln\left(\int_0^\infty \frac{pdV}{kT}\int \exp\left\{\frac{-\frac{1}{2}\sum_{i,j=1}^{nm}\frac{q_iq_j}{|x_i-x_j|} - pV}{kT}\right\}\cdot\frac{dx_1\ldots dx_{n+m}}{n!m!\Lambda^{3(n+m)}}\right) \tag{2}$$

where the thermal de Broglie wavelength $\Lambda = h/\sqrt{2\pi MkT}$, $M = M_+ = M_-$. The value of Λ does not effect the equilibrium averages including the internal energy since the contribution of Λ in $G(n, m, p, T)$ is expressed by a trivial term $(n + m)kT\ln\Lambda$. In our calculations the value of Λ was specified by a particular choice of ion mass ($M = 10$).

The Gibbs free energy is obtained in our calculations by the summation of (1).

$$G(n, m, p, T) = \sum_{\substack{k=1,l=0\\ k-l=\{0,1\}}}^{k=n,l=m} \mu(k, l, p, T) = \mu(1, 0) + \mu(1, 1) \tag{3}$$

$$+ \mu(2, 1) + \mu(2, 2) + \ldots \tag{3}$$

Values of interionic energy were also calculated. In the stationary open ensemble method [13] the particle number can have only two values. If we calculate $\mu(n, m, p, T)$, the particle numbers are either (n, m) and $(n, m - 1)$, for $n = m$, or (n, m) and $(n - 1, m)$ for $n = m + 1$. So the values of the mean configurational energy $\langle E(n, m)\rangle_{N_pT}$ and $\langle E(n, m - 1)\rangle_{N_pT}$ could be estimated by the direct Markov chain averaging over microstates with (n, m) and $(n, m - 1)$ correspondingly in the first case and $\langle E(n, m)\rangle_{N_pT}$ and $\langle E(n - 1, m)\rangle_{N_pT}$ - in the second case. This way we get an additional information on the accuracy of calculations: for instance, values of $E(2, 1)$ were obtained both in $\mu(2, 1)$ and $\mu(2, 2)$ calculations (see the Table).

b) For $n = 1$, $m = 1$, $G(n, m)$ in (2) includes a 7-dimensional integral which can be reduced to 2-dimensional one by introducing polar coordinates centred at the ion pair centre of mass. After integration over angles we get:

$$G(1, 1, p, T) = -kT\ln\left(\frac{p^*\pi^2}{\Lambda^6}\int_1^\infty D^2 dD e^{-p^*D^3}\int_1^D dx e^{1/xkT}(2x^2D^3 - 3x^3D^2 + x^5)\right) \tag{4}$$

where x is the interionic distance, $D = (6V/\pi)^{1/3}$, $p^* = \frac{1}{6}\pi(p/kT)$.

Values of the integral (4) have been obtained by expansion of the exponent and further integration of the series. Nonideal part of the internal energy $E(1, 1, p, T)$ is obtained from (4) by differentiation:

$$E(1, 1, p, T) = kT\left(-T\frac{\partial}{\partial T}\Big|_{p/T=\mathrm{const}}\left(\frac{G(1, 1, p, T)}{kT}\right) - 3\right) \tag{5}$$

G and E determined in this way are being compared with the MC results in the Table. Coincidence of both estimations extends almost up to the forth decimal figure, therefore we stopped (relatively long) MC calculations and restricted ourselves to direct estimations according to equations (4), (5).

3 DETERMINATION OF THERMODYNAMIC POTENTIALS OF CLUSTERS

The specific definition of a cluster denotes a certain way of division of the variables' space $(x_1 \ldots x_{n+m}, V)$ into a number of regions. Each of the regions corresponds to the specific division of the system into physical groups - clusters. The boundaries between these regions in principle can be varied. However the "most adequate" determination of a cluster should include a certain simplifying approximation. In fact the cluster approach denotes the account for the main contributions into the partition function.

The cluster expansion of the NpT - ensemble partition function for a macroscopic ion system in FB approximation is (see [10]).

$$\exp\left(-\frac{G(n, m)}{kT}\right) = \sum_{\{\nu_{kl}\}} \frac{\left(\sum\limits_{k,l} \nu_{kl}\right)!}{\prod\limits_{k,l} (\nu_{kl})!} \prod_{k,l} \exp\left\{-\nu_{kl}\frac{G_{cl}(k, l)}{kT}\right\} \tag{6}$$

Here $G_{cl}(k, l)$ - the Gibbs free energy of a cluster with k positive and l negative ions at fixed temperature and pressure. Equations of the type (6) for a system with small number of ions $n = 1 \ldots n_{\max}$, $m = 1 \ldots m_{\max}$ could be considered as a closed system of equations with respect to functions $G_{cl}(k, l)$ if the functions $G(n, m, p, T)$ are known.

Let us accept a preliminary assumption that clusters of the size with $k > n_{\max}$, $l > m_{\max}$ give vanishing contributions to the partition function of the macrosystem. Then the partition function of the macrosystem can be expressed according to (6) through $G_{cl}(k, l, p, T)$, $k \leqslant n_{\max}$, $l \leqslant m_{\max}$ which are to be determined preliminary from the mentioned above equations (6) for small systems.

The advantage of such an approach over the explicit determination of a cluster is that clusters introduced in such a way do not interact according to their definition. It is due to (6) (being considered as an exact system of equations) that the residue contributions into $G(n, m, p, T)$ regarded in earlier approaches as intercluster interaction effects here are completely included into $G_{cl}(k, l, p, T)$.

MC calculations for ion systems with periodic boundary conditions [1,2] show that in the region of strong nonideality there occurs intensive clustering of ions and there exists a vast region where ion pairs and triads prevail over clusters of greater size. Therefore in this region only the Gibbs potential of pairs and triads: $G_{cl}(1, 1)$ and $G_{cl}(2, 1)$, ($G_{cl}(1, 2) = G_{cl}(2, 1)$ as a result of symmetry of the system) is relevant. For determination of Gibbs potentials let us write down the first three equations of type (6), first of which is trivial:

$$\begin{aligned}
&1.\quad \exp(-\beta G(1, 0)) = \exp(-\beta\mu_0)\\
&2.\quad \exp(-\beta G(1, 1)) = \exp(-\beta G_{cl}(1, 1)) + 2\exp(-2\beta\mu_0))\\
&3.\quad \exp(-\beta G(2, 1)) = \exp(-\beta G_{cl}(2, 1)) +\\
&\qquad 2\exp(-\beta(G_{cl}(1, 1) + \mu_0)) + 3\exp(-3\beta\mu_0)
\end{aligned} \tag{7}$$

Here $\beta = (kT)^{-1}$, $\mu_0 = -kT\ln(kT/p\Lambda^3)$ - chemical potential of a monomer in the ideal mixture. We neglect a vanishing contribution of clusters with strong deviations from electroneutrality $|k - l| > 1$. In equations (7) we have in fact an implicit definition of clusters $(k, l) = \{(1, 0), (1, 1), (2, 1)\}$.

Values of $G(k, l, p, T)$ in the left side of (7) are calculated by the stationary open ensemble MC method according to the procedure described in the previous section. Reversion of the equations (7) enables us to obtain $G_{cl}(k, l, p, T)$ and hence μ_{cl}. For $p < 10^{-4}$, $T = 0.077$ the partition function for a cluster of three ions formally calculated from (7) has a negative value. Physically it means that at low pressures the ion pairs completely "squeeze off" triads - clusters of three ions are absent and

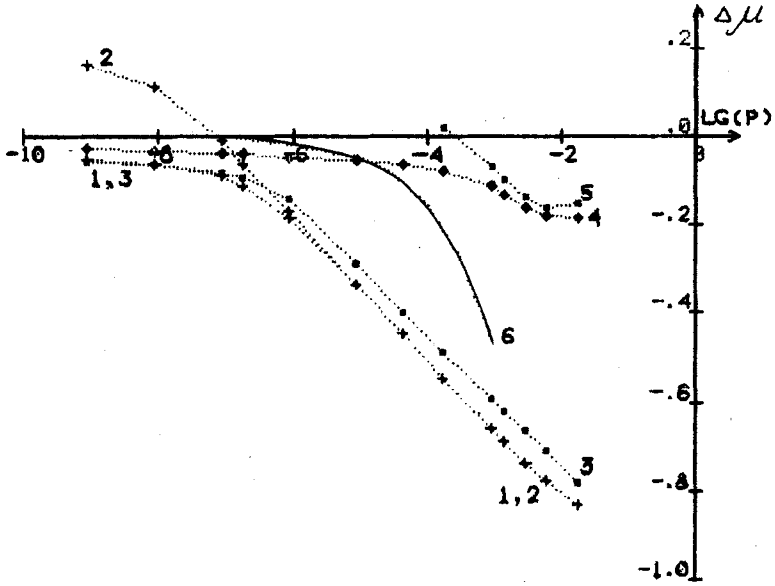

Figure 1 Nonideal part of chemical potential $\Delta\mu = \mu - \mu_0$ for small systems ($\Delta\mu(k, l)$) and clusters ($\Delta\mu_{cl}(k, l)$), for $T = 0.077$ isotherm as a function of pressure p (μ_0 - chemical potential of ideal gas). $\Delta\mu(k, l)$ - MC calculations by stationary open ensemble method [13], $\Delta\mu_{cl}(k, l)$ - calculated according to (7), $\Delta\mu_D$ - Debye-Huckel dependence. 1 - $\Delta\mu(1, 1)$, 2 - $\Delta\mu_{cl}(1, 1)$, 3 - $\Delta\mu(2, 2)$, 4 - $\Delta\mu(2, 1)$, 5 - $\Delta\mu_{cl}(2, 1)$, 6 - $\Delta\mu_D$.

consequently the third equation of (7) reduces to the two preceding ones. So at low pressures we restrict ourselves to the first two equations, i.e. to pair correlations. It is evident that the development of multiparticle correlation effects would be expressed in the increase of the number of equations in the system (7).

The computational results for $\mu_{cl}(1, 1)$ and $\mu_{cl}(2, 1)$ are presented in the Table and in Figure 1. $\mu_{cl}(1, 1, p, T)$ and $\mu(1, 1, p, T)$ coincide with each other as the pressure rises. This result can be considered as evidence of formation of stable clusters of (1, 1) composition (ion pairs). The characteristic feature of the charged particle system is that the formation of stable clusters (1, 1) occurs long before condensation. It corresponds to the results of direct MC calculations [2].

Applying operations of type (5) to the equations (7), we obtain a system of equations for the potential part of the internal energy of clusters:

$$\begin{aligned}
&1.\quad E(1, 0) = 0\\
&2.\quad E(1, 1) = \left(E_{cl}(1, 1)\exp\left(-\frac{G_{cl}(1, 1)}{kT}\right)\right)\Big/\exp\left(-\frac{G(1, 1)}{kT}\right)\\
&3.\quad E(2, 1) = \left(E_{cl}(2, 1)\exp\left(-\frac{G_{cl}(2, 1)}{kT}\right)\right)\\
&\qquad + \left(2E_{cl}(1, 1)\exp\left(-\frac{G_{cl}(1, 1) + \mu_0}{kT}\right)\right)\Big/\exp\left(-\frac{G(2, 1)}{kT}\right)
\end{aligned} \tag{8}$$

Table 1 Numerical results for isotherm $T = 0.077$ at pressures $10^{-10} < p < 10^{-1}$.

p	$-\mu_0$	$-\mu(1, 1)$	$-\tilde{\mu}(1, 1)$	$-\mu_{cl}(1, 1)$	$-\mu(2, 1)$	$-\mu_{cl}(2, 1)$	$-\mu(2, 2)$	$-E(1, 1)$	$-\tilde{E}(1, 1)$	$-E_{cl}(1, 1)$
8.90*10−10	1.589	1.640	1.647	1.428	1.618		1.647			
8.90*10−10	1.412	1.474	1.475	1.301	1.447		1.475	0.067	0.066	0.63
8.90*10−08	1.235	1.323	1.327	1.245	1.273		1.315	0.219	0.203	0.57
1.77*10−07	1.182	1.292	1.290	1.242	1.219		1.280	0.317		0.61
8.90*10−07	1.057	1.240	1.240	1.224	1.107		1.197	0.628	0.63	0.77
8.90*10−06	0.880	1.214	1.215	1.212	0.934		1.164	0.816		0.84
4.40*10−05	0.757	1.205	1.207	1.204	0.819		1.154	0.854		0.87
1.77*10−04	0.650	1.200	1.200	1.200	0.729	0.632	1.138	0.868		0.87
8.85*10−04	0.526	1.187	1.188	1.187	0.639	0.591	1.116	0.880	0.88	0.88
1.41*10−03	0.491		1.182	1.182	0.621	0.585	1.112	0.904		0.90
2.83*10−03	0.436		1.173	1.173	0.594	0.571	1.099	0.904		0.90
5.80*10−03	0.381		1.159	1.159	0.559	0.541		0.903		0.90
1.77*10−02	0.295		1.125	1.125	0.481	0.446		0.909		0.91

p	$-E^*(2, 1)$	$-E^{**}(2, 1)$	$-E_{cl}(2, 1)$	$-E(2, 2)$	$2\gamma(1, 0)$	$\gamma(1, 1)$	$2\gamma(2, 1)$	μ	μ_{MC}	V
8.90*10−10					0.971	0.029				8.92*10 07
8.90*10−10	0.079	0.047		0.068	0.947	0.053				8.89*10 06
8.90*10−08	0.283	0.246		0.356	0.812	0.198		0.09	0.089	9.58*10 05
1.77*10−07	0.368	0.442		0.712	0.179	0.281		0.16	0.156	4.18*10 05
8.90*10−07	0.675	0.652		1.089	0.485	0.515		0.26	0.245	6.36*10 04
8.90*10−06	0.838	0.807		1.566	0.206	0.794		0.37	0.346	5.51*10 03
4.40*10−05	0.882	0.858		1.672	0.104	0.896		0.41	0.396	1000
1.77*10−04	0.936	0.940	1.10	1.751	0.054	0.911	0.038	0.42	0.436	178
8.85*10−04	1.178		1.25		0.026	0.919	0.056	0.43	0.507	26.4
1.41*10−03	1.118		1.25		0.022	0.912	0.066	0.44	0.534	12.4
2.83*10−03	1.157		1.25		0.016	0.902	0.082	0.44	0.557	8.59
5.80*10−03	1.190		1.27		0.012	0.901	0.088	0.44	0.588	5.56
1.77*10−02	1.230		1.31		0.008	0.918	0.074	0.45	0.626	3.66

$\mu(k, l)$, $\mu_{cl}(k, l)$ – chemical potentials of small systems and clusters;
$E(k, l)$, $E_{cl}(k, l)$ – configurational energy of small systems and clusters;
$\gamma(k, l)$ – relative concentrations of clusters in macrosystem;
μ_{MC}, μ – specific configurational energy of the macrosystem (*MC*, [2]) and due to cluster expansion (12);
V – specific volume [2];
$E^*(2, 1)$ calculated in runs with $k = 1, 2$; $l = 1$ (together with $\mu(2, 1)$);
$E^{**}(2, 1)$ calculated in runs with $k = 2$, $l = 1, 2$ (together with $\mu(2, 2)$;
$\tilde{\mu}(1, 1)$ according to (4);
$\tilde{E}(1, 1)$ according to (5).

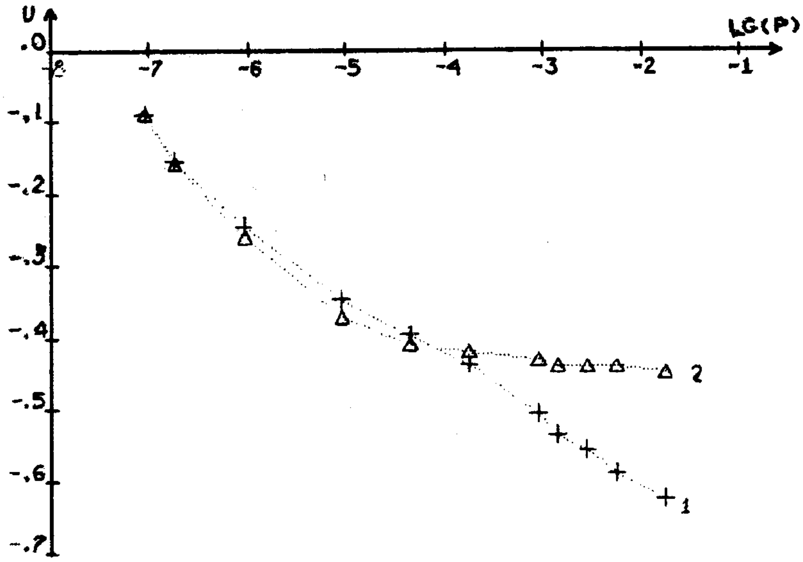

Figure 2 Nonideal part of the internal energy of plasma (per 1 ion) for $T = 0.077$ as a function of p. 1 - direct MC calculations [2], 2 - cluster expansion (12) including ion triads.

We calculated $E_{cl}(k, l)$ using MC data for $E(k, l)$ by reversion of the system (8). Computer results for $E_{cl}(k, l)$ and $E(k, l)$ are presented in Table 1. $E_{cl}(2, 1)$ has physical meaning (due to above-mentioned reasons) only for $p > 10^{-4}$.

4 CLUSTER EXPANSION FOR THE ENERGY OF THE MACROSYSTEM

The equilibrium concentrations of clusters in the macrosystem correspond to the maximal term in (6) with respect to $\{\nu_{kl}\}$ sets. These values are determined by the Lagrange variation of (6) over values of ν_{kl} [10].

$$\gamma_{kl} = \gamma_{1,0}^{k+l}\exp(-\beta(G_{cl}(k, l) - (k + l).\mu_0)) \tag{9}$$

Here $\gamma_{nm} = \nu_{nm}/\sum_{k,l}\nu_{kl}$ relative concentrations of clusters:

$$\gamma_{1,0} + \gamma_{0,1} + \gamma_{1,1} + \gamma_{2,1} + \gamma_{1,2} + \gamma_{2,2} + \dots = 1 \tag{10}$$

Formula (9) could be expressed in terms of volume concentrations $\rho_{kl} = \nu_{kl}/\langle V\rangle$ using the ideal gas equation of state $\sum_{k,l}\nu_{kl} = p\langle V\rangle/kT$:

$$\rho_{kl} = \rho_{1,0}^{k+1}\exp(-\beta G^c_{cl}(k, l))\Lambda^{3(k+l-1)} \tag{11}$$

where $G^c_{cl} = G_{cl} + kT\ln(kT/p\Lambda^3)$ is Gibbs free energy of a cluster with the fixed centre of mass. A seeming dependence of the equilibrium concentrations ρ_{kl} on Λ is actually absent since both dependences in (11) compensate each other.

Definition of a cluster in the canonical ensemble (NVT) yields, instead of (11), a well known action mass law with the Helmholtz free energy in the right side [10].

Restricting ourselves to ion pairs and triads, we obtain a closed system of equations to determine $\gamma_{1,0}$, $\gamma_{1,1}$, $\gamma_{2,1}$.

The specific (per ion) configurational internal energy of the ion plasma in the present formalism is:

$$u = \frac{\sum_{k,l} E_{cl}(k, l)\gamma_{kl}}{\sum_{k,l}(k + l)\gamma_{kl}} = \frac{E_{cl}(1, 1)\gamma_{1,1} + 2E_{cl}(2, 1)\gamma_{2,1}}{2\gamma_{1,0} + \gamma_{1,1} + 2\gamma_{2,1}} \tag{12}$$

Numerical results for the energy according to (12) are compared (Table 1 and Figure 2) with the direct MC calculation for the periodical system [2]. The coincidence within the statistical error is up to $p \sim 10^{-4}$, therefore FB approximation is adequate for $p < 10^{-4}$. The condensation apparently begins for $p > 10^{-4}$ (the shape of curve 1 changes) and FB approximation becomes unuseful.

5 CONCLUSION

It should be pointed out that the proposed approach being relatively simple yields an opportunity to describe the properties of the strongly nonideal ion plasma for a wide range of parameters without explicit account of intercluster correlational effects.

Properties of the macrosystem are expressed through using the characteristics of small systems calculated with the aid of a specific MC procedure. Consecutive augmentation of the small system enables us to check the clusterisation process. Development of multiparticle correlations is expressed by the increase of the number of nonreducing equations in the system (6).

In computer experiments on small systems we do not usually deal with a single cluster but with a mixture of clusters. Determination of cluster characteristics from MC data for small systems by means of reversion of the equation system (6) could be useful for the correct calculation of the nucleation rate.

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