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DIAGRAMMATIC APPROACH TO GAS-LIQUID PHASE TRANSITION IN STATISTICAL THEORY

In frameworks of equilibrium statistical mechanics it is proposed the analytic algorithm of sequential approximations construction when the pressure is calculated in the lattice gas model. The pressure is assumed as the function that depends on the temperature and the particle density. The algorithm is built on the basis of the virial expansion. The obtained thermodynamic function describes the gas-liquid phase transition such that the density depending on pressure has the jump if the temperature value is less than the critical one. The algorithm permits to calculate system phase diagrams together with the critical point. The formula of the pressure obtained at zero approximation corresponds to well-known average field approximation.

Keywords: lattice gas, interaction potential, partition function, fugacity, chemical potential, virial expansion, phase transition.

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ДИАГРАММНЫЙ ПОДХОД В СТАТИСТИЧЕСКОЙ ТЕОРИИ ФАЗОВОГО ПЕРЕХОДА ГАЗ-ЖИДКОСТЬ

В рамках формализма равновесной статистической механики предлагается аналитический алгоритм построения последовательных приближений для вычисления давления в модели решеточного газа как функции от плотности числа частиц и температуры. Алгоритм строится на основе известного в статистической механике вириального разложения. Получаемая на основе применения такого алгоритма термодинамическая функция описывает фазовый переход газ-жидкость так, что плотность как функция от давления испытывает скачок при температуре ниже критической. Алгоритм позволяет вычислять фазовые диаграммы системы вместе с критической точкой. Получаемая в нулевом приближении формула для давления соответствует известному приближению среднего поля.

Ключевые слова: решеточный газ, потенциал взаимодействия, статистическая сумма, активность, химический потенциал, вириальное разложение, фазовый переход

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ДИАГРАМНИЙ ПІДХІД У СТАТИСТИЧНІЙ ТЕОРІЇ ФАЗОВОГО ПЕРЕХОДУ ГАЗ-РІДИНА

В рамках формалізму рівноважної статистичної механіки пропонується аналітичний алгоритм побудови послідовних наближень для обчислення тиску в моделі решіткового газу як функції від щільності числа частинок і температури. Алгоритм будується на основі відомого в статистичній механіці віріального розвинення тиску за степенями щільності частинок ρ . Отримана на основі застосування такого алгоритму термодинамічна функція описує фазовий перехід газ-рідина так, що у неї є критична точка при зміні температури. При цьому при температурі нижче за

критичну, в залежності щільності від тиску, є стрибок. Запропонований алгоритм дозволяє обчислювати за допомогою розкладання за спеціальним малим параметром v фазові (P, T) – і (ρ, T) – діаграми системи разом з критичною точкою. З фізичної точки зору цей параметр дорівнює відношенню радіуса взаємодії до радіуса кореляцій. Математично, параметр вводиться в модель решіткового газу за допомогою приписування кожній діаграмі Майєра без вершин зчленування ваги, пропорційного підходящого степеня параметра v . Для побудови розвинення за степенями v існує потреба в апріорній інформації про значення хімічного потенціалу, при якому відбувається фазовий перехід. Воно дорівнює середній величині взаємодії пробної частинки з усією іншою системою. Цей факт раніше встановлений Лі і Янгом для систем з потенціалами тяжіння. Він є наслідком теореми про розташування нулів статистичної суми за параметром активності z . У даній роботі показано, що це справедливо для будь-якого потенціалу, що підсумовується.

Отримана в нульовому наближенні за параметром v формула для тиску відповідає наближенню самоузгодженого поля. Знайдена формула для тиску в наступному наближенні, яке пропорційне першому степеню v . На її основі отримуються поправки до критичної температури, величини стрибка щільності і до форм кривих фазових (P, T) – і (ρ, T) – діаграм. При цьому, природно, виявляється заборона на існування фазового переходу в одновимірній системі.

Ключові слова: решітковий газ, потенціал взаємодії, статистична сума, активність, хімічний потенціал, віріальне розвинення, фазовий перехід.

Problem Statement

Statistical theory of gas-liquid phase transition has the large history, but now we have no a mathematically rigorous method in frames of statistical mechanics for calculation of some thermodynamic characteristics of the transition even for such simple systems of statistical physics as gases consisting of one-atom spherically symmetric molecules. In this communication we point out the way of formulated problem solving. Namely, we propose the algorithm for the phase (P, T) -diagram evaluation using the so-called lattice approximation on the basis of the statistical mechanics formalism. This diagram represents the first order phase transition line which has the critical point. Besides, it permits to calculate the particle density ρ as a function on the pressure P such that the function has the jump.

Analysis of Recent Researches and Publications

Let we study thermodynamic system characteristics as functions on intensive thermodynamic parameters. From mathematical point of view, phase transitions are manifested in analytical expressions of these functions in the form of some essential singularities. But, at first sight, there is not such a situation in frames of statistical mechanics formalism. Beginning from the famous L. Onsager work [1], it is clear that such singularities appear as a result of so-called *thermodynamic limit* which represents the necessary stage of calculation. Works of Lie and Yang [2, 3] have pointed out the concrete mathematical mechanism according to which such singularities appear when we describe the gas-liquid phase transition. Moreover, they have shown that we cannot consider thermodynamic functions characterizing different thermodynamic phases as functions connected with each other by an analytical continuation procedure. In connection with this fact, there is a prejudice that it is impossible to study the gas-liquid phase transition by means of so-called virial expansion, i.e. by series on ρ powers. But, from other side, one may think that coefficients of the expansion named *irreducible integrals* are the full collection of system characteristics at the thermodynamic limit.

Description of Main Material of Research

1. The lattice approximation. We propose the solution of the problem which is set in the introduction having based on the *lattice approximation*. We use such an approximation because it permits to simplify essentially the solution of sufficiently routine problem which is concerned of molecule volume exclusion. Such a procedure is necessary in order to take into account of molecules rough repulsion at short distances. Let molecules may occupy only the discrete point collection $\Lambda = \{\mathbf{x} \in \mathbf{R}^3 : \mathbf{x} = a(n_1\mathbf{e}_1 + n_2\mathbf{e}_2 + n_3\mathbf{e}_3)\}$ in the cube $\Omega(\Lambda)$ with the edge aL , a is the lattice constant, \mathbf{e}_j , $j=1,2,3$ makes up a fixed orthogonal basis in \mathbf{R}^3 such that L^3 is the number of possible points of molecule space locations $|\Omega(\Lambda)| = (aL)^3$ is the system volume. Let us consider the lattice system of statistical mechanics (see, for example, [4]) with the Hamiltonian

$$H[\rho] = -\mu \sum_{\mathbf{x} \in \Omega(\Lambda)} \rho(\mathbf{x}) + \sum_{\{\mathbf{x}, \mathbf{y}\} \in \Omega(\Lambda)} U(\mathbf{x} - \mathbf{y}) \rho(\mathbf{x}) \rho(\mathbf{y}), \quad (1)$$

where μ is the chemical potential, $U(\mathbf{z})$ is the central symmetric interaction potential. To account the rough molecules repulsion, we put $U(0) = \infty$. Here, $\rho(\mathbf{x})$ is an arbitrary dichotomous function defined on lattice sites Λ . So, it has the values 0, 1. The interaction potential $U: \Lambda \mapsto \mathbf{R}$ is supposed as the summable one,

$$\|U\| \equiv \sum_{0 \neq \mathbf{z} \in \Lambda} |U(\mathbf{z})| < \infty. \quad (2)$$

On the basis of the Hamiltonian (1), the Gibbs probability distribution $P[\rho(\mathbf{x})]$ is introduced on the space $\{\rho(\mathbf{x}) \in \{0,1\} : \mathbf{x} \in \Omega(\Lambda)\}$ of elementary events. According to this,

$$P[\rho(\mathbf{x})] = Z^{-1} \exp(-H[\rho]/T)$$

is the probability of the random realization $\rho(\mathbf{x})$, where T is the statistical temperature (the Boltzmann constant is equal 1),

$$Z = \sum_{\{\rho(\mathbf{x})\}} \exp(-H[\rho]/T)$$

is the partition function. The pressure of lattice gas is defined by the formula

$$P = T \ln Z / |\Omega(\Lambda)|. \quad (3)$$

We assign the definite collection $X_n = \{\mathbf{x} : \rho(\mathbf{x}) = 1\}$ to each function $\rho(\mathbf{x})$ with $n = \sum_{\mathbf{x} \in \Omega(\Lambda)} \rho(\mathbf{x})$. Components of the collection are mismatched and they are defined with an accuracy to component permutations. Then, the partition function has the form

$$Z = \sum_{n=0}^{\infty} \frac{z^n}{n!} \sum_{X_n \in \Omega^n(\Lambda)} V_n(X_n),$$

where $V_n(X_n) = \exp\left(-\sum_{\{j,k\} \subset I_n} U(\mathbf{x}_j - \mathbf{x}_k)/T\right)$ are Boltzmann's functions. These functions equal to zero when any pair of X_n -collection components are coincide, $z = e^{\mu/T}$ is the fugacity parameter. So-called *group expansions* of the pressure and the particle density on z -powers are fulfilled [4]

$$P/T = \sum_{n=1}^{\infty} z^n b_n, \quad \rho = \sum_{n=0}^{\infty} z^{n+1} (n+1) b_{n+1}.$$

They are differed from group expansions connected with continuous systems such that integrals on particle locations are changed on summations on their discrete locations in sites of the cube lattice Λ , i.e.

$$b_n = \frac{1}{n!} \sum_{X_{n-1} \in \Lambda^{n-1}} \sum_{G \in G_n} \prod_{\{j,k\} \in G} W(\mathbf{x}_j - \mathbf{x}_k). \quad (4)$$

Here, the internal summation is done on all connected graphs G with n marked vertexes (Mayer's graphs). In formulas (4) each group coefficient $b_n(T)$ has the thermodynamic limit. This fact is connected with summability of the Urcell function $W(\mathbf{z}) = e^{-U(\mathbf{z})/T} - 1$ is summable. It is due to the summability of the potential.

Let the function $P(\rho, T)$ denotes the pressure defined by Eq.(3). It is represented by series on density powers,

$$P(\rho, T)/T = \rho \left(1 - \rho \frac{d}{d\rho} \sum_{n=1}^{\infty} \frac{\rho^n}{n+1} \beta_{n+1}(T) \right), \quad (5)$$

where coefficients $\beta_n(T)$, $n \in \mathbf{N}$ are named the irreducible integrals. They are defined by the formula

$$\beta_n(T) = \frac{1}{n!} \sum_{X_n \in \Lambda^n} \sum_{G \in F_{n+1}} \prod_{\{j,k\} \in G} W(\mathbf{x}_j - \mathbf{x}_k), \quad n \in \mathbf{N}.$$

This formula is analogous to that corresponds a continuous space molecule distribution, but integrations over all space molecule positions are changed by summations. The internal summation is done on all connected graphs without contact vertexes (see, for example, [5]). By the same way, it is fulfilled the analogous formula for the fugacity [6]:

$$z = \rho \exp\left(-\sum_{n=1}^{\infty} \beta_n \rho^n\right).$$

2. The algorithm of sequential approximations. Construction of sequential approximations is based on the use of the expansion (5). It is necessary to determine them for all collection of coefficients $\beta_n(T)$, $n \in \mathbf{N}$. Approximations are built by the introducing a supplement "small" parameter ν into irreducible integrals. From physical view-point, the parameter ν corresponds to the ratio r_0/r_c where r_c is the correlation radius and r_0 is the interaction one. Since the rough repulsion of particles is not small, we define new Urcell function:

$$W(\mathbf{z}) = \hat{W}(\mathbf{z}, r_0) - \delta_{\mathbf{z},0}$$

with the aim of approximations building. The particle volume is excluded in it. Let us consider that the function $\hat{W}(\mathbf{z}, r_0)$ is small at $r_0^{-1} \ll 1$. Then irreducible integrals $\beta_n(T)$ are represented in the form:

$$\beta_n(T) = \frac{1}{n!} \sum_{G \in F_{n+1}} \sum_{G' \subset G} (-1)^{|G'|} \beta_n(G, G', r_0), \tag{6}$$

$$\beta_n(G, G', r_0) = \sum_{X_n \in \Lambda^n} \left(\prod_{\{j,k\} \in G'} \delta_{\mathbf{x}_j, \mathbf{x}_k} \right) \left(\prod_{\{j,k\} \in G \setminus G'} \hat{W}(\mathbf{x}_j - \mathbf{x}_k, r_0) \right).$$

The internal summation in Eq.(6) is done on all subgraphs of the graph G . The particle volume exclusion in coefficients $\beta_n(T)$ corresponds to summations using Kronecker's symbols. Due to the introducing of the function $\hat{W}(\mathbf{z}, r_0)$, two kinds of edges appear in the graph G . Namely, the symbols $\delta_{\mathbf{x}_j, \mathbf{x}_k}$ correspond dotted edges \cdots , and the functions $\hat{W}(\mathbf{x}_j - \mathbf{x}_k)$ correspond continuous edges --- . The graph G' is made up of dotted edges. It represents by some subgraphs G_1, G_2, G_3, \dots , $G' = G_1 \cup G_2 \cup G_3 \cup \dots$ being not connected with each other in general case. Then, despite to fact that summations by Kronecker's symbols is simply fulfilled, in a result of summations on X_n , we obtain a complicated graph with multiple edges and contact vertexes. We name it as the *derived graph*. Thus, the summation on all derived graphs connected with all graphs G with n vertexes should be done effectively in order to calculate irreducible integrals $\beta_n(T)$. So, it takes place

Theorem 1. For each pair $\langle G, G' \rangle$, $G \in F_{n+1}$, $G' \subset G$, there is the map $N : \Sigma(G, G') \mapsto \mathbf{N}_+$ such that the following formula is fair for irreducible integrals

$$\beta_n(T) = \frac{1}{n!} \sum_{G \in F_{n+1}} \sum_{G' \subset G} (-1)^{|G'|} \sum_{X(\Sigma(G, G') \setminus \{1\}) \in \Lambda^{\Sigma(G, G')-1}} \prod_{\{j,k\} \subset \Sigma(G, G')} \hat{W}^{N(\{j,k\})}(\mathbf{x}_j - \mathbf{x}_k, r_0)$$

where $\Sigma(G, G')$ is the set of derived graph vertexes.

For each derived graph with the pair $\langle G, G' \rangle$, we calculate the asymptotic of its contribution to corresponding irreducible integral $\beta_n(T)$ when $r_0 \rightarrow \infty$, in order to determine the dependence on ν of irreducible integrals $\beta_n(T)$,

$$\beta_n(G, G', r_0) \sim \frac{(-T)^{-\kappa(G, G')}}{(r_0^3)^{m(G, G')}} \int_{(\mathbf{R}^3)^{\Sigma(G, G')-1}} \prod_{\{j,k\} \subset \Sigma(G, G')} \hat{U}^{N(\{j,k\})}(\mathbf{x}_j - \mathbf{x}_k) dX(\Sigma(G, G') \setminus \{1\}),$$

where $\kappa(G, G') \equiv \sum_{\{j,k\} \subset \Sigma(G, G')} N(\{j,k\})$ is the edge number of derived graph with the account of their multiplicity, $m(G, G') = |\Sigma(G, G')| - 1 - \kappa(G, G')$ is the characteristic indicator of derived graph.

On the basis of this result, we prescribe the multiplier $\nu^{m(G,G')}$ to each term $\beta_n(G,G')$. So, irreducible integrals are some functions on ν ,

$$\beta_n(\nu, T) = \frac{1}{n!} \sum_{G \in F_{n+1}} \sum_{G' \subset G} (-1)^{|G'|} \nu^{m(G,G')} \beta_n(G, G'), \quad \beta_1(\nu, T) = \beta_1,$$

$$\beta_n(G, G') = \sum_{X(\Sigma(G,G'), \{k_i\}) \in \Lambda^{\Sigma(G,G')-1}} \prod_{\{j,k\} \subset \Sigma(G,G')} \hat{W}^{N(\{j,k\})}(\mathbf{x}_j - \mathbf{x}_k).$$

Thus, we have defined the immersion of lattice gas model into more wide class of models which is parametrized by the analytic ν -dependence. It permits to study quantitatively the lattice gas system by means of asymptotic expansions on ν . Herewith, the original system is obtained at $\nu = 1$.

3. The location of phase transition. We propose two important statements which are necessary for construction of ν -expansions. They connected with the determination of phase transition point location. At first, it is necessary to define the relationship between z and ρ at this point. It is done on the basis of the equation:

$$\rho = z(T) \exp\left(\sum_{n=1}^{\infty} \beta_n(T) \rho^n\right). \tag{7}$$

The partition function Z is a polynomial on the fugacity z . According to the Lie-Yang theorem, all zeroes of are located on the circle with the radius $\lambda^{-1}(T)$ if the interaction potential have no positive values. Here,

$$\lambda^2(T) = \exp\left[-\sum_{\mathbf{x} \in \Lambda} \hat{U}(\mathbf{x})/T\right].$$

Zeroes fill out densely the circle arc after the passage to the thermodynamic limit when the polynomial power tends to infinity. The arc does not intersect the real axe. The phase transition is occur in the system when this arc occupies the circle completely. Naturally, the point with real value is excluded. Consequently, the value $z(T)$ is equal to $\lambda^{-1}(T)$ at $T < T_c$ when the phase transition occur. We have proved a generalization of the Lie-Yang conjecture for the case when the potential U is not attractive completely. At such a case, one cannot assert that zeroes are located on a circle. But, we have proved that they make up the set that may adjoin to real axe only in the point $\lambda^{-1}(T)$.

Theorem 2. Let $p(z, T) = T \ln Z / |\Omega|$. Then this function satisfies functional equation

$$p(z, T) = p([\lambda^2(T)z]^{-1}, T) + T \ln z - \square \hat{U} \square / 2$$

at each $T > 0$.

Consequence. The solution $\rho(z)$ of Eq.(7) satisfies functional equation

$$\rho(z) + \rho([\lambda^2(T)z]^{-1}) = 1.$$

At that it is allowed that $\rho(z)$ may be discontinuous function.

From this functional equation one may find

Theorem 3. *If there are not some critical points in the temperature interval (T_c, T_*) which are differed from T_c , then the jump of the function $\rho(z)$ may occur only at the value $z = \lambda^{-1}(T)$.*

Following statements are proved on the basis of the symmetry between completed and empty sites.

Theorem 4. *The value $\rho = 1/2$ belongs always to the interval $[\rho_-(T), \rho_+(T)]$ of the density $\rho(z)$ jump at any temperature $T < T_c$ if there is only one phase transition in the system.*

Consequence 1. *The critical value ρ_c of the density is equal $1/2$.*

Consequence 2. *The value $p(T)$ of the pressure corresponding to the jump is determined by the formula*

$$p(T) = P(1/2, T). \quad (8)$$

4. Zero approximation. To calculate the pressure in the system at zero approximation $P^{(0)}(\rho, T) = \sum_{n=0}^{\infty} \beta_{n+1}(0) \rho^{n+1}$ according to above described procedure, it is necessary to find all pairs $\langle G, G' \rangle$ which define derived graphs with the characteristic indicator $m(G, G') = 0$. It is proved that such pairs are $\langle G, \emptyset \rangle$ where G is the graph with unique continuous edge and all pairs with $n \geq 2$ which have $G' = G$, $G \in F_{n+1}$, $n \in \mathbf{N}_+$, i.e. all their edges in G are dotted. It is not complicated to prove the combinatorial formula being valid for graphs with dotted edges:

$$\sum_{G \in F_{n+1}} (-1)^{|G|} = -(n-1)!, \quad n \geq 1.$$

Taking into account the contribution into the coefficient $\beta_1(T)$ connected with the unique graph with continuous edge and summing all contributions of graphs with dotted edges, we obtain

$$T^{-1} P^{(0)}(\rho, T) = -\ln(1-\rho) - \frac{\rho^2}{2} \sum_{\mathbf{x} \in \Lambda} (e^{-\hat{U}(\mathbf{x})/T} - 1). \quad (9)$$

This expression corresponds to the *self-consistent field* approximation. In particular, at such an approximation, the pressure has the following form for the model with *the nearest-neighbors interaction* (the Ising model)

$$\hat{U}(\mathbf{z}) = -U_0, \text{ at } |\mathbf{z}| = a; 0, \text{ at } |\mathbf{z}| \neq a,$$

$U_0 > 0$, $a > 0$ is a lattice constant,

$$T^{-1} P^{(0)}(\rho, T) = -\ln(1-\rho) - 3\rho^2 (e^{U_0/T} - 1)$$

The expression (9) has the bifurcation point $\langle \rho_c, T_c \rangle$ when the temperature T is varied. Two equalities $\partial P^{(0)} / \partial \rho = 0$, $\partial^2 P^{(0)} / \partial \rho^2 = 0$ are fulfilled simultaneously at this point.

From these equations, we find that $\rho_c = 1/2$ and, moreover, we find the equation determining the temperature T_c . It has the form

$$\sum_{\mathbf{x} \in \Lambda} (\exp(-\hat{U}(\mathbf{x})/T) - 1) = 4. \quad (10)$$

It is valid the following assertion.

Theorem 5. *If the interaction potential U has negative values at some points of the lattice Λ , so there is unique critical point $T_c > 0$ that is the solution of Eq.(10).*

In particular, the equation (10) takes the form $4 = 6(e^{U_0/T} - 1)$ for the above-mentioned Ising model. It has the explicit solution $T_c = U_0 [\ln(5/3)]^{-1}$.

At zero approximation the phase (P, T) -diagram is found on the basis of Eq.(8):

$$p(T) = T \ln 2 - \frac{1}{8} T \sum_{\mathbf{x} \in \Lambda} (e^{-\hat{U}(\mathbf{x})/T} - 1).$$

Such a function $p(T)$ possesses the following properties.

Theorem 6. *The function $p(T)$ is concave and it monotonically increases at the segment $[T_*, T_c]$ where T_* is defined by the condition $p(T_*) = 0$. The point T_* is the unique solution of the equation:*

$$8 \ln 2 = \sum_{\mathbf{x} \in \Lambda} (e^{-\hat{U}(\mathbf{x})/T} - 1).$$

Particularly, for the Ising model, we obtain:

$$p(T) = T \ln 2 - \frac{3}{4} T (e^{-U_0/T} - 1).$$

At last, extreme points $\rho_{\pm}(T)$ of the density jump that takes place at the pressure value $p(T)$, are determined by extreme solutions of the equation:

$$p(T) = P^{(0)}(\rho_{\pm}(T), T),$$

that is equivalent to the equation:

$$-\ln(1 - \rho_{\pm}(T)) - \frac{1}{2} (\rho_{\pm}^2(T) - \frac{1}{4}) \sum_{\mathbf{x} \in \Lambda} (e^{-\hat{U}(\mathbf{x})/T} - 1) = \ln 2.$$

The function $\rho_-(T)$ monotonically increases on temperature and the function $\rho_+(T)$ monotonically decreases.

Asymptotic of the jump value has been calculated explicitly at small temperature deviations $\Delta = T_c - T > 0$ from the critical point:

$$\rho_+(T) - \rho_-(T) = \alpha \frac{\sqrt{\Delta}}{T_c}, \alpha > 0.$$

Thus, the critical exponent of the order parameter, i.e. the critical exponent of the jump value is equal to 1/2. It is in agreement with the Landau thermodynamic theory of second order phase transitions.

5. Correlation approximation. Such a term corresponds to first order approximation on the parameter ν :

$$P^{(1)} / T = -\rho^2 \frac{d}{d\rho} Q^{(1)}(\rho, T), \quad Q^{(1)}(\rho, T) = \sum_{n=2}^{\infty} \frac{\rho^n}{(n+1)} \beta_{n+1}^{(1)}, \quad (11)$$

since in this case the pair correlation function does not vanish. To calculate the coefficients

$$\beta_n^{(1)} = \frac{1}{n!} \sum_{G \in F_{n+1}} \sum_{G' \subset G: m(G, G')=1} (-1)^{|G'|} \beta_n(G, G'),$$

$$\beta_n(G, G') = \sum_{X(\Sigma(G, G') \setminus \{1\}) \in \Lambda^{\Sigma(G, G')-1}} \prod_{\{j, k\} \subset \Sigma(G, G')} \hat{W}^{N(\{j, k\})}(\mathbf{x}_j - \mathbf{x}_k),$$

it is necessary to describe the class of pairs $\langle G, G' \rangle$, $G \in F_{n+1}$, which generate the derived graph with the characteristic indicator $m(G, G')=1$. It is proved that such graphs are represented in the ring form. Such rings are made up of continuous edges and their “effective vertexes” are represented by some arbitrary graphs of dotted edges which have no any contact vertexes. It is necessary to find the description of all such graphs. In a result of solution of this combinatorial problem, by summation of contributions $\beta_n(G, G')$ of graphs with fixed vertex number $n \geq 2$, one may find the coefficients:

$$\beta_n^{(1)} = \sum_{s=3}^{n+1} \sum_{m=2}^{s-1} \frac{(-1)^{s-m} (n+1) \binom{s-1}{m} (n-m)!}{2(n+1-s)! (s-m)!} \sum_{X_{m-1} \in \Lambda^{m-1}} \prod_{t=1}^m (e^{-\hat{U}(\mathbf{x}_t - \mathbf{x}_{t+1})/T} - 1), \quad (12)$$

The series (11) with coefficients (12) is summated explicitly. Taking into account the expression $P^{(0)}(\rho, T)$, in a result, the formula of the pressure is obtained with the accuracy of the first order:

$$\frac{1}{T} P(\rho, T) = -\ln(1-\rho) - \frac{\rho^2}{4} \sum_{\mathbf{x} \in \Lambda} (e^{-\hat{U}(\mathbf{x})/T} - 1)(3 - e^{-\hat{U}(\mathbf{x})/T}) -$$

$$-\frac{a^3}{16\pi^3} \rho^2 \frac{d}{d\rho} \rho^{-1} \int_{\bar{\Lambda}} \ln(1 - \rho(1-\rho) [\bar{W}(\mathbf{k})]) d\mathbf{k}, \quad \bar{W}(\mathbf{k}) = \sum_{\mathbf{x} \in \Lambda} (e^{-\hat{U}(\mathbf{x})/T} - 1) e^{-i(\mathbf{k}, \mathbf{x})}$$

Here, we use the sum of triple Fourier series of the Urcell function. The formula represents the periodic function on the space \mathbf{R}^3 of wave vectors \mathbf{k} . The function period is the so-called Brillouin zone $\bar{\Lambda} = [-\pi/a, \pi/a]^3$ of inverted lattice corresponding to the simple cubic lattice $\Lambda = \{\mathbf{x} = a(n_1\mathbf{e}_1 + n_2\mathbf{e}_2 + n_3\mathbf{e}_3); n_j = 0, 1, 2, 3, \dots\}$.

On the basis of the obtained expression it has been calculated the correction of first order for the critical temperature,

$$\delta T^{-1} = -\frac{\nu}{2} \left[\sum_{\mathbf{x} \in \Lambda} \hat{U}(\mathbf{x}) \exp(-\hat{U}(\mathbf{x})/T_c) \right]^{-1} \left[\sum_{\mathbf{x} \in \Lambda} (e^{-\hat{U}(\mathbf{x})/T} - 1)^2 + \frac{a^3}{\pi^3} \int_{\Lambda} \frac{\bar{W}(\mathbf{k})(4\bar{W}(\mathbf{k})-3)}{(4-\bar{W}(\mathbf{k}))^2} d\mathbf{k} \right], \quad (13)$$

where $T = T_c$ in the integrated expression and, therefore, $T = T_c$ in the Urcell function \hat{W} i.e. $\bar{W}(0) = 4$.

Then, the convergence of the integral should be understood according to the main sense.

Strictly, it has been calculated the correction $\delta p(T)$ of the phase transition point $p(T)$,

$$T^{-1} \delta p(T) = T^{-1} P^{(1)}(1/2, T) = \frac{1}{16} \sum_{\mathbf{x} \in \Lambda} (e^{-\hat{U}(\mathbf{x})/T} - 1)^2 - G_1(1/2),$$

$$G_1(1/2) = \frac{a^3}{16\pi^3} \int_{\Lambda} \ln(1 - \bar{W}(\mathbf{k})/4) d\mathbf{k}.$$

At last, corrections of jump extreme points are found with the same accuracy:

$$\delta \rho_{\pm}(T) = \frac{1}{4} \frac{\rho_{\pm}(T)(1 - \rho_{\pm}(T))}{1 - (1 - \rho_{\pm}(T))\rho_{\pm}(T)\bar{W}_0} \times$$

$$\times \left[\frac{a^3}{4\pi^3} \int_{\Lambda} \frac{(1 - \rho_{\pm}(T))^2 \bar{W}(\mathbf{k})}{1 - \rho_{\pm}(T)(1 - \rho_{\pm}(T))\bar{W}(\mathbf{k})} d\mathbf{k} + (1 - 2\rho_{\pm}(T)) \sum_{\mathbf{x} \in \Lambda} (e^{-\hat{U}(\mathbf{x})/T} - 1)^2 \right].$$

Conclusions

Firstly, we note that one may calculate the pressure $P(\rho, T)$ by the analogous way with any accuracy on ν -powers. It may be done by evaluation of functions $P^{(k)}(\rho, T) = -\rho^2 (dQ^{(k)} / d\rho)$, with coefficients $\beta_n^{(k)}$ being proportional to ν^k , $k = 2, 3, \dots$. The phase transition of first order is manifested by first two approximations. Secondly, we point out that the expression under the integral defining $P^{(1)}(\rho, T)$ exists only in the case when the following conditions are fulfilled

$$\rho(1 - \rho)W^{(m)} < 1, \quad W^{(m)} = \max_{\mathbf{k} \in \Lambda} \{\bar{W}(\mathbf{k})\}.$$

Thus, the function $P(\rho, T)$ has the natural domain

$$\rho < \rho_-^{(m)} \equiv \frac{1}{2} \left(1 - (1 - 4/W^{(m)})^{1/2} \right), \quad \rho > \rho_+^{(m)} \equiv \frac{1}{2} \left(1 + (1 - 4/W^{(m)})^{1/2} \right).$$

at the approximation pointed out. By other words, the inverse function that represents the dependence of ρ on P has the jump by the natural way at this approximation.

Besides, we note that $\delta T = \infty$, if the formula (12) of the correction δT is applied formally for the one-dimensional case. Thus, the self-consistent field approximation (averaged field approximation) is not correct. This fact is very important since the application of this approximation caused doubt in statistical physics due to the fact that it predicts the phase transition for one-dimensional systems, but it is known the statement that phase transitions are absent in one-dimensional systems with summated interaction potential [4].

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