GAS-LIQUID PHASE TRANSITION IN STATISTICAL MECHANICS

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Abstract

A new theory on gas-liquid phase transition is given. The new idea is that the total intermolecular potential energy for a classical system in equilibrium is relative with the average distance of molecules. A new space homogeneity assumption is postulated, a new formulation — the mean distance expansion, instead of Mayer’s Cluster Expansion, is introduced, a new explanation on liquid-gas phase transition is given, and the physical quantities in a system of coexistent vapor and liquid — the densities of the coexistent vapor and liquid, the vapor pressure and the latent heat, are calculated.

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I. INTRODUCTION

In my recent paper [1], a new theory to discuss first order gas-liquid phase transition in statistical mechanics is given. The basic idea is the following: 1) A new Space Homogeneity Assumption (SHA) is postulated: In a classical system in equilibrium with volume $V$, particle number $N$, when gravity and boundary effects are omitted, each particle occupies volume $V/N$ averagely. The SHA is quite different from Eyring’s assumption (it is referred as EHSA SHA later) [2]: the number of the particles in a volume $d^3r$ is $N/V4\pi r^2 dr$. We will demonstrate in detail later that the SHA, in contrast with EHSA SHA, will exhibit the correlation between the mean distance of molecules and the partition function. 2) In order to calculate the intermolecular potential and the partition function for a classical system, a new formulation — mean distance expansion, instead of Mayer’s cluster expansion [3], is introduced, which is characterized by the intermolecular mean distance $\bar{r} = (V/N)^{1/3} = (1/n)^{1/3}$, as a parameter, appearing in the expressions of the intermolecular potentials and the partition functions. This implies that the intermolecular potentials and the partition functions are dependent on the intermolecular mean distance. Thus the derivatives of partition functions (some thermodynamic functions) will be relative to the intermolecular mean distance. 3) A new explanation on first order gas-liquid phase transition in statistical mechanics is given: First order gas-liquid phase transition does not correspond to singularities of thermodynamic functions. For a given temperature $T < T_c$ and some pressure $P$, there are two densities of particle number $n_g$ and $n_l$ (densities of vapor and liquid) that satisfy the equations $P(T, n_g) = P(T, n_l)$ and $\mu(T, n_g) = \mu(T, n_l)$. In each branch thermodynamic functions, such as $\mu_g(T, n_g)$ or $\mu_l(T, n_l)$, are analytic. 4) The new theory tells us how to calculate the physical quantities in a system of coexistent vapor and liquid: densities of coexistent vapor and liquid, vapor pressure and latent heat, etc.

In this paper, we will give some concrete models, as examples, to exhibit how the new theory works. In section two, starting from the SHA and the mean distance expansion, and by using Sutherland potential, we obtain partition function of VDW fluid and coexistence of two phases is discussed. Densities of vapor and liquid, vapor pressure and latent heat for VDW fluid are also calculated. In section three, modified VDW fluid is discussed and the better results are obtained. In section four, the differences between new theory and Mayer’s cluster expansion are identified.
II. MEAN DISTANCE EXPANSION OF THE VDW FLUID

For a classical system in equilibrium, we consider the pair interaction which is only relative to the distance of particles. The potential energy between particle \(i\) and particle \(j\) is \(u(r_{ij})\), where \(r_{ij}\) is the distance of these two particles. We assume that the potential energy \(u(r_{ij})\) is shared by particle \(i\) and particle \(j\) together and is divided to these two particles equally. According to the SHA, particle \(i\) occupies a volume \(V/N = 1/n\), where \(n\) is the particle number density. For convenience, suppose that this volume is a sphere with radius \(r_1 = (3/4\pi n)^{1/3}\), and particle \(i\) is located at its center. We then draw many spherical surfaces centered by particle \(i\) outside the sphere, so that the volume of every shell formed by neighboring two spherical surfaces is \(V/N\), and we will have one particle per shell averagely. The radius \(r_j\) of the \(j'\)th sphere is determined by \(4\pi r_j^3/3 = j/n\). Then intermolecular potential energy of particle \(i\) can be expressed as

\[
U_i = \frac{1}{2} \sum_{j=1}^{N-1} u(r_j)
\]  

and the total potential energy of the system is \(U = NU_i = \frac{1}{2}N \sum_{j}^{N-1} u(r_j)\). Thus the partition function is given by

\[
Z = \frac{1}{N!\lambda^{3N}} \int \exp \left( -\frac{1}{k_BT} U \right) dq = \frac{1}{N!\lambda^{3N}} \exp \left( -\frac{N}{2k_BT} \sum_{j=1}^{N-1} u(r_j) \right) \int dq
\]

where \(\lambda\) is thermal wavelength. If the intermolecular potential is the Sutherland potential

\[
u(r) = \begin{cases} +\infty, & r < \sigma, \\ -\varepsilon(\sigma/r)^3, & r \geq \sigma. \end{cases}
\]  

We obtain the partition function of VDW fluid

\[
Z = \frac{1}{N!\lambda^{3N}} (V - Nb)^N \exp \left( \frac{1}{k_BT} aNn \right)
\]

with \(a = \sum_{j=1}^{N-1} \frac{2\pi\sigma^3}{3j}, b = \frac{2}{3}\pi\sigma^3\), and free volume \(\int dq = (V - Nb)^N\).

A. The Equation of State

The VDW equation of state is obtained as follows

\[
P = k_BT \left[ \frac{\partial}{\partial V} \ln Z \right]_{T,N} = \frac{nk_BT}{1 - nb - an^2}
\]
As well known, we have the critical data

\[ n_c = \frac{1}{3b} \]

\[ k_B T_c = \frac{8a}{27b} \]

\[ P_c = \frac{a}{27b^2} \]

\[ \frac{P_c}{n_c k_B T_c} = \frac{3}{8} \]

The reduced equation of state is

\[ P^* = \frac{8n^* T^*}{3 - n^*} - 3n^{*2} \]

with reduced quantities \( P^* = P/P_c, T^* = T/T_c \) and \( n^* = n/n_c \).

**B. Chemical Potential**

Chemical potential is expressed as follows

\[ \mu = -k_B T \left[ \frac{\partial \ln Z}{\partial N} \right]_{V,T} = -2an + k_B T \ln \left[ \frac{n}{1 - nb} \right] + \frac{n k_B T b}{1 - nb} - \frac{3k_B T}{2} \ln \frac{2\pi m k_B T}{h^2} \]

We find that the solutions of equations (12) and (13)

\[ \frac{\partial \mu}{\partial n} = 0, \]

\[ \frac{\partial^2 \mu}{\partial n^2} = 0, \]

are the same as the formulae (6)–(8). Letting

\[ \overline{\mu} = \frac{\mu}{k_B T} + \ln b + \frac{3}{2} \ln \frac{16\pi ma}{27bh^2} , \]

and substituting Eq. (11) into (14), we have

\[ \overline{\mu} (T^*, n^*) = \ln \frac{n^*}{3 - n^*} - \frac{3}{2} \ln T^* + \frac{n^*}{3 - n^*} - \frac{9n^*}{4T^*}, \]

which is a function of reduced quantities only. Now we can define the reduced chemical potential \( \overline{\mu}^* = \overline{\mu}/\overline{\mu}_c \), and draw its isotherms as shown in Fig.1.
FIG. 1: the reduced chemical potential $\pi^*$ at different temperature for VDW fluid

**C. Densities of Coexistent Vapor and Liquid**

For a coexistent gas-liquid system, we have the conditions for two phases to exist in equilibrium

$$P^* (T^*, n_g^*) = P^* (T^*, n_l^*), \quad (16)$$

$$\pi^* (T^*, n_g^*) = \pi^* (T^*, n_l^*). \quad (17)$$

From equations (10) and (16), we have

$$\frac{8T^*}{(3 - n_g^*) (3 - n_l^*)} = n_g^* + n_l^*. \quad (18)$$

From the equations (14) and (17), we have

$$4T^* \left[ \ln \frac{n_g^*(3 - n_l^*)}{n_l^*(3 - n_g^*)} + \frac{3(n_g^*-n_l^*)}{(3-n_g^*)(3-n_l^*)} \right] = 9(n_g^*-n_l^*). \quad (19)$$

The solutions of Eq. (18) and Eq. (19) given by numerical method are plotted in Fig.2. This curve is equivalent to that given by Maxwell rule in thermodynamics.

The curve in Fig.2 can be described by the empirical formulae (firstly introduced by Wei Wang)

$$n_l^* = 1 + 0.497 (1 - T^*)^{1.086} - 0.56 (1 - T^*)^{1.53} + 2(1 - T^*)^{0.5}, \quad (20)$$

$$n_g^* = 1 + 0.497 (1 - T^*)^{1.086} + 0.56 (1 - T^*)^{1.53} - 2(1 - T^*)^{0.5}. \quad (21)$$
FIG. 2: Densities of coexisting vapor and liquid: blue—the experimental curve from Guggenheim, green—VDW fluid, red—MVDW fluid. Both of red and green are the theoretical results in this paper.

\[ \frac{n_l^*-n_g^*}{2} = -0.56 \left( 1 - T^* \right)^{1.53} + 2 \left( 1 - T^* \right)^{0.5} , \]  

(22)

\[ \frac{n_l^* + n_g^*}{2} = 1 + 0.497 \left( 1 - T^* \right)^{1.086} . \]  

(23)

Formula (22) suggests the critical exponent \( \beta = 0.5 \) when \( T^* \to 1 \). Formula (23) states the well-known law of the rectilinear diameter. Comparing with the numerical values of the solutions of Eq.(18) and Eq.(19), the inaccuracy of the formula (20) is less than 0.1% when \( T^* > 0.6 \), and the inaccuracy of the formula (21) is less than 0.1% when \( T^* > 0.71 \). The percentage of inaccuracy increases as the temperature drops below \( T^* = 0.71 \).

D. Vapor Pressure

The reduced vapor pressure is expressed as

\[ P^* = \frac{8n_g^*T^*}{3 - n_g^*} - 3n_g^{*2} = \frac{8n_l^*T^*}{3 - n_l^*} - 3n_l^{*2} . \]  

(24)

Substituting Eq. (19) into Eq. (24), we obtain another expression of vapor pressure

\[ P^* = \frac{3n_g^{*2} \exp \left[ \frac{9}{4T^*} \left( n_l^* - n_g^* \right) - \frac{3}{8T^*} \left( n_l^{*2} - n_g^{*2} \right) \right] - n_l^{*2}}{1 - \exp \left[ \frac{9}{4T^*} \left( n_l^* - n_g^* \right) - \frac{3}{8T^*} \left( n_l^{*2} - n_g^{*2} \right) \right]} . \]  

(25)

Fig.3 illustrates the relation between vapor pressure and its corresponding temperature. And this relation can be expressed by the empirical formula

\[ \ln P^* = 3.5204 - 3.5660/T^*. \]  

(26)
FIG. 3: Comparison between the experimental and the theoretical results of vapor pressure. Blue— the experimental curve from Guggenheim [6], green—VDW fluid, red—MVDW fluid.

E. Latent Heat

The free energy of the system can be written as

\[ F = k_B T \ln N! - \frac{3}{2} N k_B T \ln \frac{2 \pi m k_B T}{\hbar^2} - a N n - N k_B T \ln (V - N b) . \]

The internal energy reads

\[ E = -T^2 \frac{\partial}{\partial T} \left[ \frac{F}{T} \right] = \frac{3}{2} N k_B T - a N n. \]

and then we obtain the difference between the internal energies per particle in two phases:

\[ \Delta U_i = \frac{E_g}{N_g} - \frac{E_l}{N_l} = a (n_l - n_g) = U_i (\tau_g) - U_i (\tau_l) , \]

where \( U_i (\tau_g) \) and \( U_i (\tau_l) \) are the potential energies per particle in vapor and liquid determined by equations (1), (3), (20) and (21) correspondingly, which are only dependent on mean distances in the two phases. Multiplying the Avogadro’s constant \( N_A \), we obtain the difference between the molar internal energies in the two phases

\[ \Delta U = N_A a (n_l - n_g) . \]

The first law of thermodynamics is expressed as

\[ \Delta U = \Delta Q - P (v_g - v_l) = L - P (v_g - v_l) , \]
where \( v_g \) and \( v_l \) are the molar volume of vapor and liquid respectively. And we obtain the latent heat for VDW fluid

\[
L = N_A a(n_l - n_g) + P(v_g - v_l) = N_A \left[ a(n_l - n_g) + P\left(\frac{1}{n_g} - \frac{1}{n_l}\right)\right].
\]

(32)

which is equivalent to Clapeyron’s equation (see Appendix A). We define \( \overline{L} = L/P_c v_c \) and \( \overline{L} \) can be written as

\[
\overline{L} = 3(n^*_l - n^*_g) + P^*(\frac{1}{n^*_g} - \frac{1}{n^*_l}).
\]

(33)

which is a function of reduced quantities \( P^*(T^*) \) and \( n^*(T^*) \) only. Fig.4 shows the relation between latent heat \( \overline{L} \) and temperature \( T^* \). The blue curve is drawn from experimental data of argon [4]. The green one is from Eq. (33).

III. MODIFICATION TO THE VAN DER WAALS EQUATION OF STATE

In 1945, E.A. Guggenheim [5] collected experimental data on densities of coexisting vapor-liquid for eight substances and plotted on a curve. He found that the curve could be
represented by the empirical formulae

\[
\frac{n_l}{n_c} = 1 + 0.75(1 - \frac{T}{T_c}) + 1.75(1 - \frac{T}{T_c})^{1/3}
\]  (34)

\[
\frac{n_g}{n_c} = 1 + 0.75(1 - \frac{T}{T_c}) - 1.75(1 - \frac{T}{T_c})^{1/3}
\]  (35)

It means that the critical exponent \( \beta = 1/3 \) when \( T^* \to 1 \) for real gases.

It was also E.A. Guggenheim [6] who provided the empirical formula on the equilibrium vapor pressure

\[
\ln P^* = 5.29 - \frac{5.31}{T^*}
\]  (36)

Comparing with Guggenheim’s experimental data (34)–(36), we find that the formulae (20), (21) and (26), like in the case of the latent heat (33), are right qualitatively, but not right quantitatively. The reason is that the Sutherland potential Eq. (3) corresponding to the VDW fluid does not reflect the actual interaction. In order to obtain the better results and to keep a form as simple as VDW equation, we introduce the effective potential

\[
U(r) = \begin{cases} 
+\infty, & r < \sigma, \\
-\varepsilon(s/r)^MT^S, & r \geq \sigma.
\end{cases}
\]  (37)

where \( M \) and \( S \) are constants. In the Mayer’s cluster expansion, to keep convergence we have to let \( M \geq 3 \). But in the mean distance expansion there is no such restriction.

Following the standard procedure like in section two, we have the partition function

\[
Z = \frac{1}{N!\lambda^N} \exp(\beta aT^SNn^*(1+S)/(V-Nb)^N
\]  (38)

Eq. (10) reads

\[
P^* = T^S \left[ \frac{12(3+M)n^*T^*(1-S)}{M(6+M-Mn^*)} - \frac{6+M}{M}n^*(1+S) \right]
\]  (39)

with

\[
n_c = \frac{M}{(6+M)b}
\]  (40)
\[ k_B T_c^{1-S} = \frac{4(3 + M)}{M} \left( \frac{M}{6 + M} \right)^{2 + \frac{M}{2}} ab^{-\frac{M}{4}} \]  \hspace{1cm} (41)

\[ P_c = \frac{M}{3} \left( \frac{M}{6 + M} \right)^{2 + \frac{M}{2}} \frac{a}{b^{1 + \frac{M}{4}}} T_c^S \]  \hspace{1cm} (42)

when \( M = 3, S = 0 \), the Eq. (39) is VDW equation, when \( M = 3, S = -1 \), the Eq. (39) is the Berthlot’s equation \[7\].

Eq. (11) and Eq. (15) read
\[ \mu = - \left( 1 + \frac{M}{3} \right) an^\frac{M}{n} T^S + k_B T \ln \left( \frac{n}{1-nb} \right) + \frac{n k_B T b}{1-nb} - \frac{3k_B T}{2} \ln \frac{2\pi mk_B T}{h^2}. \]  \hspace{1cm} (43)

\[ \bar{\mu} = \ln \frac{n*M}{6 + M - n*M} + \frac{n*M}{6 + M - n*M} - \frac{3}{2} \ln T^* - \frac{n*M*T^*(S-1)(6+M)^2}{12M} \]  \hspace{1cm} (44)

Eq. (24) reads
\[ T^*(1-S) = \frac{(6 + M - Mn_g^*) (6 + M - Mn_l^*)}{12 (3 + M) (n_g^* - n_l^*)} \left[ n_g^* \left( 1 + \frac{M}{n^*} \right) - n_l^* \left( 1 + \frac{M}{n^*} \right) \right] \] \hspace{1cm} (45)

Eq. (25) reads
\[ T^*(1-S) = \frac{(6 + M)^2 \left( n_g^* \frac{M}{n^*} - n_l^* \frac{M}{n^*} \right)}{12 \left[ \ln \frac{n_g^* (6+M-Mn_l^*)}{n_l^* (6+M-Mn_g^*)} + \frac{M(6+M)(n_g^*-n_l^*)}{(6+M-Mn_g^*)(6+M-Mn_l^*)} \right] M} \] \hspace{1cm} (46)

Eqs. (32) and (33) read
\[ L = N_A \left[ a T^S (1-S) (n_i^* \frac{M}{n^*} - n_g^* \frac{M}{n^*}) + P \left( \frac{1}{n_g^*} - \frac{1}{n_l^*} \right) \right] \] \hspace{1cm} (47)

\[ \bar{L} = \frac{3(6 + M)}{M^2} (1-S) T^S (n_i^* \frac{M}{n^*} - n_g^* \frac{M}{n^*}) + P^* \left( \frac{1}{n_g^*} - \frac{1}{n_l^*} \right) \] \hspace{1cm} (48)

The solutions of Eqs. (44) and (45) with \( M = 2.83 \) and \( S = -0.49 \) are plotted in Fig.2, the corresponding vapor pressure and the latent heat are shown in Fig.3 and Fig.4. All of them are better than the results of VDW fluid.

As shown in Fig.2, the curve of coexisting vapor-liquid densities for the modified VDW fluid locates between the VDW curve and Guggenheim’s experimental curve, indicating that the critical exponent \( \beta \) for the modified VDW fluid values between 1/2 and 1/3. How can
we get $\beta = 1/3$ so that it coincides with experimental data? By letting $M$ and $S$ in Eqs.(44) and (45) as the functions of $T^*$ as follows

$$M(T^*) = -1.08 \sqrt{-1 + \frac{(T^* - 0.69)^2}{0.3086^2}} \frac{0.998 - T^*}{|T^* - 0.998|} + 3.865$$  (49)

$$S(T^*) = \frac{-(4 - 4T^*)^{-0.45} + 0.92(T^* - 0.7)}{|T^* - 0.7|} - 0.38$$  (50)

we obtain densities of vapor and liquid $n_g^*$ and $n_l^*$, which almost exactly coincide with Guggenheim’s experimental curve, with $\beta = 1/3$, as shown in Fig.5.

IV. DISCUSSION

The partition function of VDW fluid was derived by J.E.Mayer and M.G.Mayer in 1940s from their cluster expansion, and by H.Eyring, D.Henderson, etc. in 1964 from their EHSA SHA. What are the differences between this paper and their works? We will find out in detail in this section.

A. The New Idea in this Work

The new idea in this work is that the total intermolecular potential energy for a classical system in equilibrium is relative to the average distance $\tau$ of molecules. It is also the key
difference between this work and Mayer’s cluster expansion theory. To demonstrate this, we draw an isotherm of the reduced pressure \( p^* \) and the reduced potential energies per particle \( U^*_i = U_i(n)/U_i(n_c) \) against the reduced densities \( n^* \), as shown in Fig.6. When the system runs from \( a \) to \( g \), or from \( l \) to \( d \), the reduced potential energies per particle will vary as \( n^* \) changes, which is completely different from Mayer’s work.

**B. Existence of Two Phases**

In a homogeneous system with a temperature \( T < T_c \) and the corresponding vapor pressure \( P \), when the number of particle is unknown, the phase in which this system exists, for example liquid phase or vapor phase, is uncertain. These different fluid phases correspond to different solutions of Eqs.(16 – 17), which form two branches of solutions of Eqs.(16 – 17).

**C. Singularities on Isotherm**

In Fig.6 on the isotherm \( a – g – l – d \) there exist singularities at the point \( g \) or \( l \). The function \( P = P(T^*, n^*) \) is not differentiable at \( g \) or \( l \) on the isotherm \( a – g – l – d \). This is due to the fact that the segments \( a – g \) and \( g – l \) in Fig.6 are described by different partition functions respectively. The segment \( a – g \) or \( l – d \) is on an isotherm of a homogeneous system, which is described by partition function (4). The segment \( g – l \) in Fig.6 describes an isotherm for an equilibrium coexisting vapor-liquid system that is not a homogeneous system and cannot be described by partition function (4). In Appendix B we give a partition function for an equilibrium coexisting vapor-liquid system, which corresponds to the segment \( g – l \).

**D. Nature of Latent Heat**

The calculation about latent heat is one of the most important parts in this paper, which provides a powerful support to the SHA — the basic assumption in this work, and distinguishes this work from previous works, for instance, Mayer’s cluster expansion and the EHSA SHA, evidently. The average distance of gas molecules is larger than that of
FIG. 6: The relation between the potential energy per particle $U^*$ and densities $n^*$. The curve a-g-b-e-l-d is an isotherm of pressure $P^*$. When pressure runs from a to g, the densities vary from $n_a^*$ to $n_g^*$, the corresponding potential energy per particle $U^*$ change from $U^*(n_a^*)$ to $U^*(n_g^*)$. The gap $U_{il}^* - U_{ig}^*$ between two phase is shown.

liquid molecules. The interaction of gas molecules and the interaction of liquid molecules can be described by the same interaction potential, such as Eq. (2). The difference between the mean distances of molecules in the two phases results in the difference of molecular potential energies in the two phases. When a liquid molecule vapors and becomes a gas molecule, there is an interaction potential energy gap between the molecules in the two phases $\Delta U = U_i(r_g) - U_i(r_l) = a(n_l - n_g)$. On the other hand, the work done by the change between the volumes per mole in the two phases is $P(v_g - v_l)$. The sum of the interaction potential energy gap and the work is equal to latent heat. This is the true physical meaning of latent heat — what Mayer’s cluster expansion and EHSA SHA have failed to point out.

E. Analytic Properties of Thermodynamic Function

From the discussion about the liquid-gas transition in this paper, we know that the gases and the liquids appear in different branches of diagram $P - n$ and diagram $\mu - n$, but yet surface tension is not taken into account. When surface tension is considered, supersaturation and supercooling may occur. The isotherm will follow $a - g - b$ or $d - l - e$ in Fig.6. On the segments $g - b$ or $l - e$, the system is not in a stable equilibrium, but still is homogeneous, and can be described by partition function (3). In these cases, thermodynamic
functions are analytic in each branch, even at the first order transition points \( g \) or \( l \).

When \( T \to T_c \), we have \( n_{g \to n_c} \) and \( n_{l \to n_c} \), the critical phenomena will appear. The coexistence of two phases given in this paper will play a very important role in critical phenomenon. We will discuss it in another paper.

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**APPENDIX A: EQUIVALENCE BETWEEN EQ. (31) AND THE CLAPEYRON EQUATION**

Eq. (31) can be written as

\[
L = U_g - U_l + P(v_g - v_l)
\]

Applying thermodynamic relation

\[
U = \mu + Ts - Pv
\]

and phase conditions

\[
P_g = P_l
\]

\[
\mu_g = \mu_l
\]

we have

\[
U_g - U_l = T(s_g - s_l) - P(v_g - v_l)
\]

then Eq. (A1) is

\[
L = T(s_g - s_l) = Ts_g - s_l(v_g - v_l)
\]

According to Maxwell relations and the characters of two phases in equilibrium

\[
\frac{\partial s}{\partial v}_T = (\frac{\partial P}{\partial T})_V
\]
\[ \left( \frac{\partial s}{\partial v} \right)_T = \frac{s_g - s_l}{v_g - v_l} \quad (A7) \]

\[ \left( \frac{\partial P}{\partial T} \right)_V = \frac{dP}{dT} \quad (A8) \]

where the linearization relation between entropy and volume of (B21) is used. Eq. (A5) yields

\[ L = T \frac{dP}{dT} (v_g - v_l) \quad (A9) \]

This is just the Clapeyron equation.

**APPENDIX B: COEXISTENT GAS-LIQUID SYSTEM**

In this part, we will debate thermodynamics and statistical mechanics of a coexistent gas-liquid system.

Considering a coexistent gas-liquid system in equilibrium with particle number \( N = N_g + N_l \), volume \( V = V_g + V_l \). For a given temperature \( T < T_c \), densities of vapor and liquid, \( n_g \) and \( n_l \), are determined by Eqs. (16) and (17). First, we examine its thermodynamics. We have

\[ dU_g = T ds_g - P dV_g + \mu dN_g \quad (B1) \]

\[ dU_l = T ds_l - P dV_l + \mu dN_l \quad (B2) \]

So

\[ dU = T ds - P dV \quad (B3) \]

where \( U = U_g + U_l \), \( S = S_g + S_l \), and \( dN_g = -dN_l \). In the same way, we have

\[ dF = -SdT - PdV \quad (B4) \]

\[ dG = -SdT + VdP \quad (B5) \]

Now we discuss statistical mechanics for VDW fluid. For the vapor and liquid parts, the partition functions are

\[ Z_g = \frac{1}{N_g!} \left( \frac{2\pi mk_BT}{\hbar^2} \right)^{\frac{3}{2}N_g} e^{\beta_s N_g n_s} (V_g - N_g b)^{N_g} \quad (B6) \]
respectively. We have

$$P_g = k_B T \left( \frac{\partial}{\partial V_g} \ln Z_g \right)_{T,N_g} = \frac{n_g k_B T}{1 - n_g b} - a n_g^2$$

(B7)

$$P_l = k_B T \left( \frac{\partial}{\partial V_l} \ln Z_l \right)_{T,N_l} = \frac{n_l k_B T}{1 - n_l b} - a n_l^2$$

(B8)

$$\mu_g = -k_B T \left( \frac{\partial}{\partial N_g} \ln Z_g \right)_{T,V_g}$$

(B9)

$$\mu_l = -k_B T \left( \frac{\partial}{\partial N_l} \ln Z_l \right)_{T,V_l}$$

(B10)

The partition function for the system is

$$Z = Z_g \cdot Z_l$$

(B11)

We then define pressure and chemical potential for the coexisting system

$$P = k_B T \left( \frac{\partial}{\partial V} \ln Z \right)_{T,N} = -a n_g n_l + \frac{n_g n_l k_B T}{n_l - n_g} \left[ \ln \left( \frac{1}{n_g} - b \right) - \ln \left( \frac{1}{n_l} - b \right) \right]$$

(B12)

$$\mu = -k_B T \left( \frac{\partial}{\partial N} \ln Z \right)_{T,V} =$$

$$-k_B T \left[ \frac{a}{k_B T} (n_g + n_l) + \frac{n_g}{n_g - n_l} \ln \left( \frac{1}{n_g} - b \right) - \frac{n_l}{n_g - n_l} \ln \left( \frac{1}{n_l} - b \right) + 1 \right]$$

$$-\frac{3}{2} k_B T ln \frac{2\pi m k_B T}{h^2}$$

(B13)

(B14)

It is easy to prove $P = P_g = P_l$ and $\mu = \mu_g = \mu_l$ if the system is in equilibrium, i.e. when we have $\mu_g = \mu_l$ and $P_g = P_l$. To do this, we only need to calculate

$$2P - P_g - P_l = \frac{n_g + n_l}{n_l - n_g} (P_g - P_l) = 0$$

(B15)

$$2\mu - \mu_g - \mu_l = \frac{2}{n_l - n_g} (P_g - P_l) = 0$$

(B16)

where $\mu_g = \mu_l$ is used.
Under the conditions $\mu_g = \mu_l$ and $P_g = P_l$ for a given temperature $T$, partition function $Z = Z_g \cdot Z_l$ has only one independent variable. Let $x = N_g/N$, then partition function can be written as

$$Z(x) = \frac{1}{(xN)!} \frac{1}{(1-x)N)!} \left(\frac{2\pi mk_B T}{b^2}\right)^{\frac{N}{2}} e^{\beta N a [x n_g + (1-x) n_l]} \frac{N^N}{N^N} (B17)$$

$$\times \left(\frac{x}{n_g} - xb\right)^{xN} \left(\frac{1-x}{n_l} - (1-x)b\right)^{(1-x)N}.$$

Next we will derive a thermodynamic relation of a coexistent gas-liquid system in equilibrium with fixed $T$ and $P$. The molar entropy of the system is

$$s = x s_g + (1-x) s_l \quad \text{(B18)}$$

where $s_g, s_l$ are molar entropy of gas and liquid respectively. From the relation

$$v = x v_g + (1-x) v_l \quad \text{(B19)}$$

we have

$$x = \frac{v - v_l}{v_g - v_l}, \quad 1 - x = \frac{v_g - v}{v_g - v_l} \quad \text{(B20)}$$

substituting Eq. (B20) to (B18), then

$$s = \frac{s_g - s_l}{v_g - v_l} v + \frac{v_g s_l - v_l s_g}{v_g - v_l} \quad \text{(B21)}$$

when $T, P$ are fixed, $s_g, s_l, v_g, v_l$ are all constant. So from this relation, we can see that entropy is the linear function of volume under the given conditions.

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