Rediscussion on gas-liquid phase transition

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Abstract

Liquid-gas phase transition in statistical mechanics is a long-standing dilemma not yet well explained. In this paper we propose a novel approach to this dilemma, by: 1). Putting forth a new space homogeneity assumption. 2). Giving a new formulation—the mean distance expansion, instead of Mayer’s Cluster Expansion, to calculate the intermolecular potential and partition function for a classical system. 3). Explaining how the separation of two phases occurs below the critical temperature \( T_c \) and what is the gap between two phases. 4). Calculating the physical quantities in a system of coexistent vapor and liquid, and comparing them with the experimental results. Qualitative, and some quantitative, consistencies are obtained. So the statistical explanation on first order liquid-gas phase transition is solved in principle.

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Gas-liquid phase transition is a fundamental problem remaining unsolved for centuries in statistical mechanics since the VDW equation of state was developed in 1873. Since then, a great deal of attention had been focused on providing statistical explanations for the separation of phases by many physicists[1-17]. This letter provides a new way to solve it. Based on space homogeneity assumption and mean distance expansion, instead of Mayer’s Cluster Expansion, to calculate the intermolecular potential and partition function for a classical system, this work at first time reveals the existence of the energy gap between two phases; offers a rational physical explanation on phase transition and latent heat; and demonstrates how to calculate physical quantities in a system of coexistent vapor and liquid: such as densities of coexistent gas and liquid, vapor pressure and latent heat, etc. As examples, we discussed gas-liquid transition for both the VDW fluid and the modified VDW fluid. The experimental results provide qualitative, and some quantitative supports to the new theory.

H.Eyring and D.Henderson etc, mentioned their space homogeneity assumption (it is referred as EHSE SHA in this paper) in their book[18]: “we shall make the unfounded assumption that the molecules are randomly distributed throughout the volume and the number of molecules lying near a particular molecule in a
concentric shell ranging from \( r \) to \( r + dr \) is \( dN = N/V4\pi r^2 dr \), with \( r \geq \sigma \)." They derived the VDW equation of state from their EHSE SHA, but the total potential energy and the partition function are independent of the mean distance of molecules in their theory.

Now we put forth a new Space Homogeneity Assumption (SHA): *In a classical system in equilibrium with volume \( V \), particle number \( N \), when gravity and boundary effects are omitted, each particle averagely occupies volume \( V/N \).* We will demonstrate in detail later that the SHA will exhibit the correlation between the mean distance of molecules and the partition function.

Both the SHA here and the EHSE SHA should be regarded as independent theoretical assumptions, which cannot be proved by statistical mechanics. Their justifications lie in the agreement between results derived from them and the experimental facts. Now we reevaluate the partition function under the SHA.

We assume that the potential energy \( u(r_{ij}) \) between particle \( i \) and particle \( j \) is shared by these two particles together and is divided between both equally. We call \( u_i = \sum_{j \neq i}^{N-1} \frac{1}{2} u(r_{ij}) \) the potential belonged to particle \( i \) if only the pair interaction exits. According to the SHA, the volume occupied by particle \( i \) is equal to \( V/N = 1/n = \bar{v} \), where \( n \) is the particle number density and \( \bar{v} \) is the mean distance of molecules. For convenience, we presume that this volume is a sphere with diameter \( d = (6/\pi n)^{1/3} = \alpha \bar{v} \) in a three-dimensional space, and particle \( i \) is at its center. We then draw many spherical shells centered by particle \( i \) outside this sphere. The thickness of each spherical shell is \( d \).

From inside to outside, we number them \( S_1, S_2 \) and so on in turn. Then the volume of the shell \( S_k \) is \( V_k = \frac{4}{3} \pi \left[ (2k+1)^3 - (2k-1)^3 \right] d^3 \) and the number of the particles in this shell is \( N_k = nV_k \). The potential energy of particle \( i \) is \( U_i = 1/2 \sum_k N_k u(r_k) \), where \( u(r_k) \) is the potential contribution of a particle in the shell \( S_k \) to particle \( i \), \( (k-1/2)d \leq r_k \leq (k+1/2)d \) and \( \sum_k N_k = N - 1 \). The total potential of the system is \( U = NU_i \). The potential energy \( u(r_k) \) can be expanded at the location \( r_k = kd \), which is the distance between the midpoint of the shell \( S_k \) and particle \( i \): \( u(r_k) = u(kd) + u'(kd)(r_k - kd) + \cdots \). If only taking the first term of this expansion, i.e. \( u(r_k) \approx u(kd) \), we have the partition function

\[
Z_0 = \frac{1}{N!\lambda^N} \exp \left( -\frac{\beta N}{2} \sum_k N_k u(kd) \right) \int dq, \tag{1}
\]

with \( \lambda \) thermal wavelength. The Eq.(1) clearly indicates that the potential (as does the partition function) of the system is correlative with the mean distance. Such a relation plays a vital role in the discussion of the phenomenon of liquid-gas coexistence. When in Eq.(1) taking the Sutherland potential: \( u(r) = \infty \) if \( r < \sigma \), and \( u(r) = -\varepsilon (\sigma/r)^3 \) if \( r > \sigma \), where \( \sigma \) is the diameter of the hard core and \( \varepsilon \) is a constant, we obtain the partition function of VDW fluid:

\[
Z_0 = \frac{1}{N!\lambda^N} \exp(\beta aN^2/V)(V - Nb)^N, \tag{2}
\]
with \( a = \sum_k N_k \varepsilon_k \), \( b = \frac{4}{3} \pi \sigma \). The VDW equation is \( P = k_B T \frac{\rho}{\partial N} \ln (Z_0)_{T,N} \).

The chemical potential of VDW fluid can be obtained by

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

Letting

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

and substituting Eq. (3) into (4), we have

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

with reduced quantities \( T^* = T/T_c \) and \( n^* = n/n_c \). The Eq.(5) is a function of reduced quantities only. Now we can define the reduced chemical potential \( \overline{\mu}^* = \mu^*/\overline{\mu}_c \). When \( T < T_c \), there are three numerical values of \( n \) corresponding to a given chemical potential \( \mu \), which forecasts the coexistence of multiple phases.

For a coexistent liquid-gas system we have the conditions of equilibrium: \( P(T, n_g) = P(T, n_l) \) and \( \mu(T, n_g) = \mu(T, n_l) \). Thus the solutions of these two equations, \( n_g = n_g(T) \) and \( n_l = n_l(T) \) (the densities of the coexistent vapor and liquid, respectively), can be obtained by a numerical method, as shown (dashed line) in Figure 1A. This curve is equivalent to that given by Maxwell rule in thermodynamics.

The dashed curve for VDW fluid in Fig.1A can be described by the empirical formulae (firstly introduced by Wei Wang)

\[
n^*_l = 1 + 0.497 (1 - T^*)^{1.086} - 0.56 (1 - T^*)^{1.53} + 2 (1 - T^*)^{0.5},
\]

\[
n^*_g = 1 + 0.497 (1 - T^*)^{1.086} + 0.56 (1 - T^*)^{1.53} - 2 (1 - T^*)^{0.5},
\]

or

\[
\frac{n^*_l - n^*_g}{2} = -0.56 (1 - T^*)^{1.53} + 2 (1 - T^*)^{0.5},
\]

\[
\frac{n^*_l + n^*_g}{2} = 1 + 0.497 (1 - T^*)^{1.086}.
\]

Formula (8) suggests the critical exponent \( \beta = 0.5 \) when \( T^* \rightarrow 1 \). Formula (9) states the well-known law of the rectilinear diameter. Comparing with the
numerical values of the solutions, the inaccuracy of the formula (6) is less than 0.1% when $T^* > 0.6$, and the inaccuracy of the formula (7) is less than 0.1% when $T^* > 0.71$. The percentage of inaccuracy increases as the temperature drops below $T^* = 0.71$.

Substituting them into VDW equation, we then get the vapor pressure $P = P(T)$. The reduced vapor pressure is expressed as

$$P^* = \frac{8n_g^*T^*}{3-n_g^*} - 3n^*_g = \frac{8n_l^*T^*}{3-n_l^*} - 3n^*_l. \quad (10)$$

as shown in Figure 1B (dashed line). Substituting $\mu^*$ into Eq. (10), we obtain another expression of vapor pressure

$$P^* = \frac{3n_g^*}{1 - \exp\left[-\frac{9}{4T^*} (n_l^* - n_g^*) - \frac{3}{4T^*} (n_l^2 - n_g^2)\right]} \exp\left[-\frac{3}{4T^*} (n_l^* - n_g^*) - \frac{3}{4T^*} (n_l^2 - n_g^2)\right]. \quad (11)$$

This relation can be expressed by the empirical formula

$$\ln P^* = 3.5204 - 3.5660/T^* \quad (12)$$

There is a gap of internal energies between the two phases. From Eq.(2) the potential energies per particle in vapor and liquid are $U_{ig} = -an_g = -1/2 \sum_k N_k u(k\alpha r_g)$ and $U_{il} = -an_l = -1/2 \sum_k N_k u(k\alpha r_l)$ respectively. The difference between the two is $dU_{gl} = U_{ig} - U_{il} = a(n_l - n_g)$, which is the gap of internal energies between the two phases due to the different mean distances, as shown in Fig.2, where $U^* = U/U_c$. The average distance of gas molecules is larger than that of liquid molecules. The interactions between gas molecules
Figure 2: The relation between the potential energy per particle and densities. The curve \( a - g - l - d \) is an isotherm of pressure \( P^* \). When pressure runs from \( a \) to \( g \), or from \( g - l \) the corresponding potential energy changes from \( U_i^*(n_a^*) \) to \( U_i^*(n_g^*) \). The gap \( U_{il}^* - U_{ig}^* \) is shown.

and the interactions between liquid molecules can be described by the same interaction potential, such as Sutherland potential. 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 vaporizes and becomes a gas molecule, there is an interaction potential energy gap between the molecules in the two phases \( dU_{gl} \). The gap exists only under the SHA and the mean distance expansion, in contrast with Mayer’s theory in which there was no gap. In fact, the partition function (2) was already formally presented in some of the previous works, but it is with different meanings and the comparable inferences on phase transition could not be arrived at as no gap existed in their discussion.

The molar latent heat can be expressed simply by

\[
L = N_A \left( dU_{gl} + Pdv_{gl} \right) = N_A \left[ a \left( n_l - n_g \right) + P \left( 1/n_g - 1/n_l \right) \right],
\]

which is equivalent to the Clapeyron’s equation[19] and \( N_A \) is Avogadro’s constant. The meaning of this formula is very clear: the mean distances between molecules are different when the system is in different phases. This difference leads to the gap of the intermolecular potential between the two phases, which together with the work done due to volume difference between two phases engenders latent heat. Other theories cannot give latent heat also. We define
\[ \bar{L} = \frac{L}{P_c v_c} \] and \( \bar{L} \) can be written as

\[ \bar{L} = 3(n_i^g - n_i^l) + P^* \left( \frac{1}{n_i^g} - \frac{1}{n_i^l} \right). \]  \qquad (14)

which is a function of reduced quantities \( P^*(T^*) \) and \( n^*(T^*) \) only. Fig.1C shows the relation between latent heat \( \bar{L} \) and temperature \( T^* \). The solid-curve is drawn from experimental data of Argon[22]. The dash-curve is the latent heat of VDW fluid from Eq.(14). The consistencies between the latent heat calculated by the Eq.(13) and that by the Clapeyron’s equation provide a strong support to the new theory in this letter.

From Figure1 we find that the densities of coexistent vapor-liquid, the vapor pressure and the latent heat of VDW fluid are qualitatively correct, but quantitatively incorrect, when compared with the experimental data[20-22]. This inconsistency is due to the incorrect potential we have chosen.

Using the effective potential \( u(r) = -\varepsilon T^S(\sigma/r)^M \) (referred to as modified VDW fluid) with \( S=-0.49 \) and \( M=2.83 \) (in Mayer’s and Eyring’s works, we should have \( M \geq 3 \) to keep convergence, but there is no such restriction in mean distance expansion), instead of the attractive potential \( u(r) \) in Sutherland potential, and following the above standard calculation procedure, we obtain the better results (see dot-line in Fig.1).

Now let us review what is new in this work. The starting point of this work is the SHA. The difference between the SHA and the previous works, such as Mayer’s and Eyring’s work, is the following: a). The EHSE SHA claimed that the number of the particles in a volume \( d^3r \) is \( dN = N/V 4\pi r^2 dr \) whereas the SHA postulates that each particle occupies a volume \( V/N \). b). Mayer and Eyring assumed that the distributions of particles are nonexclusive, i.e. the distribution of an arbitrary particle is not affected by other particles. On the contrary, the SHA postulates that the distributions of particles are exclusive, i.e. each volume element \( V/N \) can, but can only lodge one particle averagely. This is a fundamental difference between mean distance expansion and Mayer’s cluster expansion. c). The intermolecular interactions in Mayer’s and Eyring’s calculations are independent of the mean distance \( \tau \), meaning that when the mean distance or the density varies, the intermolecular interactions do not change. As a result, based on its interactions, we cannot distinguish which phase the system is in: vapor or water. But in this work, when the density of the system goes from \( n_g \) to \( n_l \), or from \( n_a \) to \( n_g \), the interaction will change as the mean distance varies.

The new idea in this work is that the total intermolecular potential energy and partition function for a classical system in equilibrium are relative to the average distance \( \overline{r} \) of molecules (or density). Starting from it, we obtain the energy gap between two phases, and a new explanation for the first order gas-liquid phase transition is given as follows: first order gas-liquid phase transition does not correspond to singularity of thermodynamic functions. In Fig.2 if a system runs from \( a-g \) on the isotherm \( a-g-l-d \), the corresponding potential energy increases as density changes. At \( g \) or \( l \), there are two possible phases with
different intermolecular potential. These different fluid phases correspond to
different solutions of Eqs. \( P(T, n_g) = P(T, n_l) \) and \( \mu(T, n_g) = \mu(T, n_l) \),
which form two branches of the solutions. For each branch \( \mu_l(T, n_l) \) or \( \mu_g(T, n_g) \),
either function \( \mu_l(T, n_l) \) or \( \mu_g(T, n_g) \) are analytic (see ref.[19] for detail). When
\( T = T_c \), we have \( n_l = n_g = n_c \) and the gap \( dU_{gl} \to 0 \). Here there is no request
for the thermodynamic limit in strict mathematical sense.

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