A survey of the liquid-crystal phase transition of a hard sphere BCC with the optimized spherical approximation based on the modified weighted density function theory and its application in color science.

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Abstract: In accordance with the weighted density function theory (WDA), another formulation for the non-uniform classical fluids has been suggested. This mentioned formula has been termed as "the modified weighted-density approximation (MWDA)". One of the first usages of this approximation and one of the primary inputs is choosing the appropriate correlated function related to the interaction of the corresponding sector. For this particular purpose, a different correlated function has been used – such as PY and PELK functions. In this part, we use crystalline solid (BCC) and the correlated function spectacularly. Indeed, for the non-uniform classical fluid, the same approximation of hard spherical molecules will be considered. Eventually, the application of practical consequences relevant to this new approach in the resin and color industries will be surveyed. Besides, we examine the new conditions from the practical perspectives.

1. Introduction

First of all, we will derive the weighted density function from the theoretical perspective. Then, the main characteristics of the BCC solid are surveyed. Afterwards, we will express how the transition of the notions of solid state physics related to the calculation of multi-phase and practical process will be done. After that, we concentrate on the main subject. Hence we investigate the phase transition of the materials with spherical molecules in a sequence. The usage of the density functional theory for survey of phase transition refers to 50`s which has been developed significantly so far. Certainly, most of researches have been conducted on the crystals with FCC structure but in this investigation, the crystals with BCC structure are studied.

2. The theoretical structure of BCC solid and the modified weighted density function theory (MWDA)

2-a. The weighted density approximation *(WDA)*

For a very little classical system, *Helmholtz* extra free energy, $F_{ex}(P)$, is a unique function of the density P, as shown in the below form:

$$f_{ex}(P) = \int \vec{dv}\ \vec{p}(r) f(\vec{v};(p)) \tag{1}$$

Where $f(\vec{v},(\vec{p}))$ shows the extra free energy of the substance. In this approximation, the extra energy is defined as follows:

$$f_{ex}{}^{WDA}(P) = \int \vec{dv}\ \vec{p}(r) f(\vec{p};(\vec{r})) \tag{2}$$

where f_0 is related to extra free energy on the particle of the uniform fluid and $\vec{p}(\vec{v})$ is the average of the weighted density for the single-particle, $p(\vec{r})$, in accordance with the weighted function $\dot{w}$, it means:

$$\int \vec{dr'}\ \vec{p}(r')\dot{w}(\vec{r} - w(\ \vec{r} - \vec{r}'\ ; \vec{p}(\ \vec{r})) \tag{3}$$

It satisfies its particular weighted function with ease.

$$\int d\vec{r'}\ w(\vec{r}' - \vec{r}\ ;\ p(r)) = 1 \tag{4}$$

Now, the correlated function is inserted. The connection between the correlated function of *n* particles and $f_{ex}(p)$ is formed by this way:

$$C^{(n)}\left(\vec{r_1}, \ldots, \vec{r_n}\ ;(p)\right) = -\beta\ \frac{\delta^2 f_{ex}(p)}{\delta p(\vec{r_1}) \ldots \delta p(\vec{r_n})} \tag{5}$$

For *n=2*:

$$c^{(2)}(\vec{r} - \vec{r}'\ ; p_0) = -\beta\ \lim_{p \to p_0} \frac{\delta^2 f_{ex}(p)}{\delta p'(\vec{r}')} \tag{6}$$

Finally, by using the conversion:

$$-\beta^{-1} c_0{}^{(2)}(x\ ;p) = 2f'_0(p_0)w(x\ ;p_0) + \tag{7}$$
$$p_0 f'_0(po)w^2(x\ ;p_0) + 2p_0 f'_0(p_0)w'(x\ ;p_0)w(x\ ;p_0)$$

The last formula is the same approximation of the weighted density which had been proposed by *Achcroft*.

2-b. The modified weighted density approximation *(MWDA)*

In WDA, used approximation $f(\vec{r};(p))$ determines the extra free energy on the particle. But in the modified weighted density approximation, the formulation concentrated on the extra free energy on the particle will be in this form: $fex(p)/N$ where N is the number of particles in the system. It is obvious that $f_{ex}(p)/N$ in comparison with $f(\vec{r},(p))$ does not depend on the conditions. We show this approximation with p'. Indeed, it is independent of the place which makes it different from $\overline{p}(\vec{r})$. So, *MWDA* is a method which could measure $f_{ex}(p)/N$.

Thus, we will have:

$$f_{ex}^{MVDA}(P)/N = f_0(\hat{p}) \tag{8}$$

$$\hat{p} \equiv \frac{1}{N}\int d\vec{r}\ p(\vec{r})\int d\vec{r}'\ p(\vec{r})\ \tilde{w}(\vec{r}-\vec{r}';\hat{p})$$

And the weighted function satisfies the circumstance of interaction, again.

$$\int d\vec{r}'\ w(\vec{r}-\vec{r}';\hat{p}) = 1 \tag{9}$$

By combining two mentioned formulas -number 6 and 9- where *V* is termed as the volume of the system. By using the direct Fourier conversion, We will arrive at this:

$$\tilde{w}(x;p_0) = \frac{-1}{2f'_0(p_0)}\left[B^{-1}c_0^{(2)}(x;p_0) + \delta_x p_0 f_0 o''(p_0)\right] \tag{10}$$

Clearly, this formula is the modified weighted density approximation.

2-c. BCC solid

So as to use the modified weighted density approximation in surveying the interaction of gas-liquid- solid, the weighted density of the corresponding solid should be calculated first. Hence the attributes of BCC crystals must be considered in brief. Then, the function of its weighted density $\hat{p}$ will be computed in Fourier space. By doing this task through the formula $\hat{p}$, the collective integrals are converted into the sum of the vectors of the reverse solid network.

In a nutshell, there exists around fourteen types of network molecular arrangement or cellular structure. A large number of metals and most of the other solids possess molecular structure in shapes of body-centered cubic (BCC), face centered *cubic* (FCC) and hexagonal *closed* packed (HCP).

In BCC system, there is an atom on each of eight corners and in the intersection of diameters. Each of the eight corners of the cube is a corner of other cubes. Therefore, 1/8 of the atom in the cube, will be the corresponding share. It means that the coordination number of the atom is 8 and the share of each unit will be 12 full-atom. One of them is the central atom and another one is the result of 8 of 1/8 atom located on the corners.
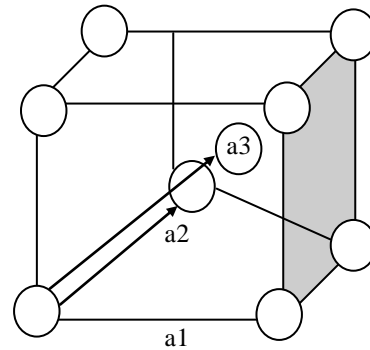

Figure 1. BCC Solid network vectors

The reverse space or the n-dimensional space is the one which the Fourier conversion function is defined for a specific function(as an illustration, the frequency domain is defined in a space with the Fourier conversion for a time-dependent function) Fourier conversion transforms us from the main space to reverse one, and vice versa. Generally, we have:

$$f(\vec{x}) = \int_{-\infty}^{\infty} f(\vec{r})e^{-i\vec{x}.\vec{r}}\ d^3r \tag{11}$$

The reverse space is a different set of points in this space and the vector of $\vec{x}$ is the maker of the image connected to the major space. *Brillouin* zone in this space is the volume which includes all the unit vectors with the periodic structure itself. So as to calculate on the bases, we will show the Fourier conversion as follows:

$$f\vec{\sigma} = N\int dv\ n(\vec{r})\exp(i\vec{\sigma}.\vec{r}) = NS\sigma \tag{12}$$

Where N is named as the number of crystal cells. When $\vec{r} = o$ is matching with one of unit atoms located on the corners, we can write the electron distribution:

$$n\,(\vec{r}) = \sum n_j\,(\vec{r} - \vec{r}_j) \qquad (13)$$

By expressing the structural function as the sum over all atoms in the cell, we will arrive at:

$$s\vec{\sigma} = \sum_j f_j \exp[-i\,2\pi\,(hx_j + xy_j + hz_j) \qquad (14)$$

In the above formula, f_j is the atomic coefficient and $\vec{r_j} = x_j\vec{a_1} + y_j\vec{a_2} + z_j\vec{a_2}$ is the vector of the main network and $\vec{\sigma} = h\vec{b_1} + h\vec{b_2} + h\vec{b_3}$ is the reverse network vector. Now, for instant, we are going to survey the connection between the reverse network vectors and main ones of BCC and FCC crystals. The former ones are smaller than the latter. As an illustration, for BCC solid with the fixed network number a, this amount for the reverse space of the FCC solid will be $\frac{4\pi}{a}$. So, the shortest vector of the reverse network from one corner to the center of adjacent face will be the below amount:

$$\left(\frac{4\pi}{a}\right)(1.2\,,\,1.2\,,\,0)$$

For example for Iron, by the final length $2\sqrt{2\pi}/a$, we have: $a = 3.59\,A°$ and the length of the reverse network vector is 24.8 nanometers.

To compute the functional fixed number for each particular network, we have to do the summation upon all atoms in the unit cell and since the crystals are often described in terms of *Miller* indices, so we also use them for calculations.

As far as we know, the BCC system is described as a simple cubic one with these vectors $a\,\hat{z},\,a\,\hat{y}\;\;a\,\hat{x}$ and a primary assumption; $\vec{r_1} = \frac{a}{2}\,(\hat{x} + \hat{y} + \hat{z})$ and $r_0 = 0$. Clearly, its reverse network is the same simple cubic system with the network constant number $2\pi/a$. In a single-atom crystal, all structural functions f, are the same. The intensity of the scattered beam together with this vector, $x = \frac{2\pi}{a}\left(h\hat{x}^* + xy^* + l\hat{z}^*\right)$ from this surface (hkl) is shown as:

$$f_x = f\left[e^{-i\,\vec{x}.\vec{o}} + e^{-i\vec{x}.\left(\frac{a}{2}\right)(\hat{x} + \hat{y} + \hat{z})}\right]$$

$$= f\left[1 + e^{-i\vec{x}.\left(\frac{a}{2}\right)(\hat{x} + \hat{y} + \hat{z})}\right]$$

$$= f\left[1 + e^{-i\pi\,(h + k + l)}\right]$$

$$= f\left[1 + (-1)^{h + k + l}\right] \qquad (15)$$

Thus, the structural constant for the surface (hkl) is indicated as follows:

$$F_{hkl} = \begin{cases} 2f & , & h + k + l \quad \text{even} \\ o & , & h + k + l \quad \text{odd} \end{cases} \qquad (16)$$

It means, in order to create the reflection in the diffraction experiment for a BCC crystal, the sum of the indices connected to the surface should be even. If the sum of the Miller indices is odd, The intensity of the beam will be scattered and will reach zero. Besides, the interference would be destructive and the zero status in the intensity happens alternatively. The most intensity of diffraction occurs in BCC solid on surface (110).

3. Collecting data and consequences

In this part, we attempt to put the density distribution function relevant to BCC crystal into the theory and then calculate *Helmholtz* free energy. But prior to this, it is rational that some of the theoretical and practical results of this method should be explained and at least we must know that what kind of results we are looking for in the end. The formulation of the Interface between a solid and liquid has been always controversial. From the experimental perspective, contact of two surfaces is related to two condensed matters. It is obvious that acquiring the contact information throughout using practical methods directly, appears to be a little difficult. Therefore, in this situation indirect parameters are measured. As an illustration, these two states of condensed matters adjacent together, make another kind of material as a result of the interactions and their influence on each other. But from the theoretical view, contact mechanism is considered to be the same for both materials. From this point, interaction between solid and liquid is divided into two categories: the first one is the solid in a liquid of the same material, in this state, the

structural changes should be surveyed. The second one is related to the liquid and solid which are not the same, in this case, thermodynamic and chemical behavioral differences are studied.

Atomic modeling provides specific condition to simulate both phases and it also aids us to find a nearly direct approach so that the atomic interactions with ease. *Kerbekht* model and *Lennard-Jose* model can be good samples of the mentioned approach.

In this equation, $\emptyset_w(z)$ is termed with the interacted potential between tough sphere and the surface.

a

b

Figure 2. Interaction potential due to the crystal surface in term of the surface 111 and 100

Figure 3. Density profile in term of distance. a: surface (100), b: surface (111)
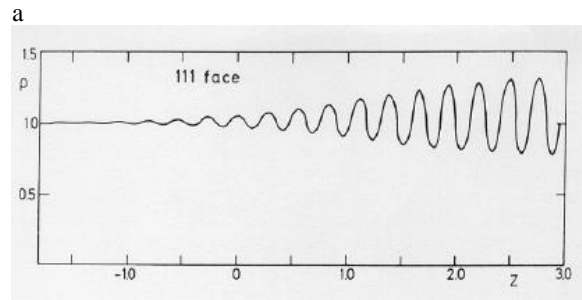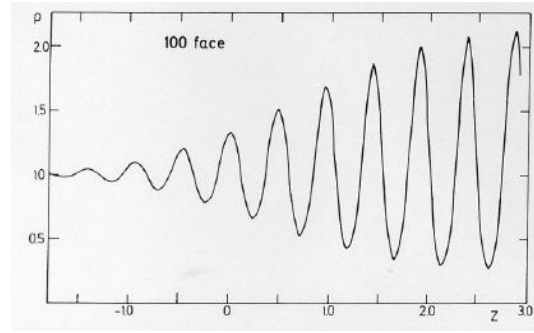
As we mentioned before, the density function of solid-fluid system in Fourier analysis and based on the wave vector - K_n - in the reverse space of the solid network is introduced as follows:

$$\rho(v) = \rho_0(1+n) + \rho_0 \sum_n \mu_n \exp(ikn.r) \qquad (17)$$

In the above formula, $\{x_n\}$ is the sum of the reverse vectors in solid network, n is the coefficient of density variation during solidification and μ_n is Fourier coefficients.

In fact, all vectors of reverse network in the mentioned series will not be existed. So, those vectors which are the closest neighbors will be considered. It happens because the role of the farther vectors in density is less effective.

Comparing profiles of surfaces (111) and (100)in BCC solid, it is concluded that it would be alternative significantly and the approximation of interaction between fluid phase and other various layers is also obtained. If the density of fluid is $v(\rho($ and the density of fluid-like is $\rho(e)$, just under this circumstance: $\Delta\rho << 1 \cdot \Delta\rho = \rho(v) - \rho(e)$, jump density could be ignored near the iced point of fluid. Furthermore, if $\Delta\rho$ changes slightly, it could be concluded that the vibrations of the density declines by increasing the distance and it is eliminated with the distance ξ from the surface. It means that the existence of the solid contributes to the process of internal changes in fluids to be done fast.

Since we are not going to check the consequences, we complete this issue by discussing the graph related to the interaction of solid BCC and liquid. Based on figure 4, we could recognize what processes happen at the zero point- the boundary of solid substance.
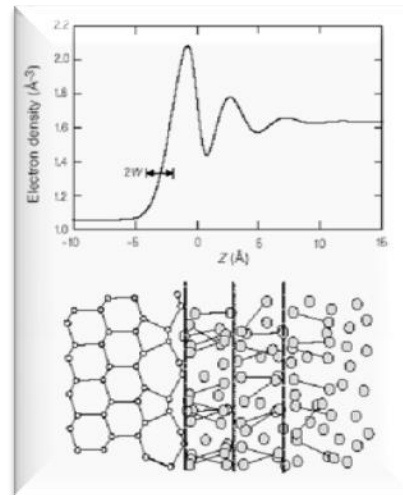

Figure 4. The curve of electron density in terms of distance

In this section, we are going to illustrate a suitable instant related to the interaction between

faces 111 and 110, then the differences are checked. For face 110 at 99 degrees Celsius(it is exactly 1 degree below the melting point), we poured one drop of Aluminum on the surfaces 110 and 111. The drop contains 861 solid particles and 16 layers. It is witnessed that the melting point for the final surface is much more smooth in the below interaction. At the higher temperature of the melting point, because of phase changes and also in accordance with the time which is required more to complete the interaction, the attained surface is rougher that the previous state. This matter will be discussed in the applications section.
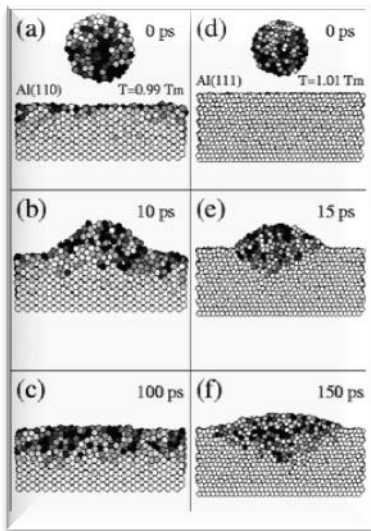

Figure 5. Schematic image of interaction in Aluminum close to its melting point.

Density profile $\rho(z)$ as the average density of particles along the length Δz in parallel to the solid surface and z is defined as the length of the spot. The sub-surface is divided into two physical layers. The function of density profile is:

$$\rho(z) = \frac{< N_z >}{L_x L_y \, L_z} \qquad (18)$$

Where $L_x L_y$ is the dimension of the cell in directions x and y, so that it will be perpendicular on direction z and L_z is the length of the middle part. $< N_z >$ is the number of particles which are located between $z - \frac{\Delta z}{2}$ and $z + \frac{\Delta z}{2}$ in the period t, the average value will be the average time. Potential function of each particle is introduced as follows:

$$U_p = \sum_{i \in \ell} u_i / N(L) \qquad (19)$$

Where $N(L)$ presents the quantity of atoms belonging to the layer, u_i is the amount of interaction energy relevant to the particle i and finnally, L is the sum of the all particles in the layer. So, the temperature of each layer could be calculated from the equation:

$$T = \frac{2E_x^\ell}{3N(L)x_B} = \frac{1}{3N(L)\,x_B} \sum_{i \in \ell} \left| \vec{v}_i^{\,2} \right| \qquad (20)$$

Where Ex^ℓ is the kinetic energy of layer L and $\vec{v}_i$ is the velocity of the particle i. In the calculations, units are taken into account that the mass of the particle is assumed one. Thus, $\vec{v}_i$ would be the same momentum. Now, parameter $S(x)$ is defined as follows:

$$S(x) = \sum_{ij \in \ell} e^{i\vec{x}\,\vec{v}_i} \, |2/N(L)|^2 \qquad (21)$$

In the above equation, x is the vector of the reverse network. We can now calculate the radial distribution function of two-dimensional with ease. Certainly, we know that the radial distribution function of three-dimensional is the below form:

$$\rho g(v) = < \sum_{ij \in \ell} \delta(r - v_{1j}, \Delta v)/v\left(\vec{v}_i, v, \Delta r\right) >/N(L) \qquad (22)$$

v_i is the atom location i, $r_{ij} = \left| \vec{v}_i - v_j \right|$ is its displacement, p is the volumetric density and $v\left(\vec{v}_i, v, \Delta r\right)$ is the spherical coplanarity *with the* center r_i and diameter v and thickness Δr and $<>$ is the average time on the concurrent routes and δ is the same Kronecker delta.

If you assume that h_n is the number of atoms which are in the form of (i, j) in n of this layer, it means that they are the ones which are true under this circumstance $(n-1)\Delta v < v_{ij} < n\Delta v$. The mentioned function at the point $r_n = \left(n - \frac{1}{2}\right)\Delta v$ will be in the below form

$$g(r_n) = \frac{V(L)h_n}{2\pi N(L)^2 r_n^2 \Delta r} \qquad (23)$$

By the replacement $A(L)$ instead of $V(L)$, this below equation is obtained:

$$(24)$$

Now, the results of the calculation concerning solid BCC are described briefly below:

The profile of density for (*100*) BCC−A at three alternative temperature has been shown in figure 6 and the diagrams relevant to *(110)* BCC−A are plotted in figure 7. Where, the rate of changes is constant and the density of the average numbers of two layers to the density of the liquid is transitioning. Anyway, it is remarkable that in BCC (100), the first peak of the liquid happens approximately $0.615Å°$ from the surface continuously. This occurrence is indicated more accurately in figure 8. The first two peaks are related to the solid. In addition, another high peak is witnessed so close to them.
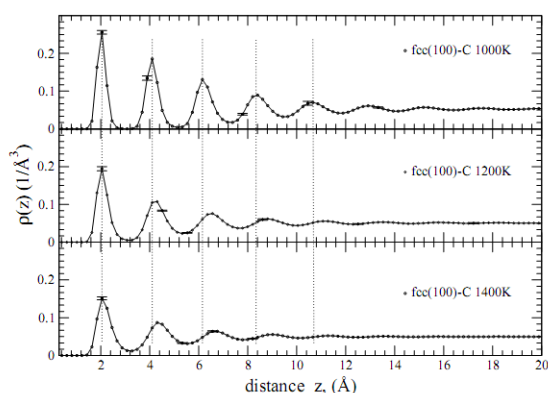

Figure 6. The diagram of density function for FCC solid based on distance at various temperatures.
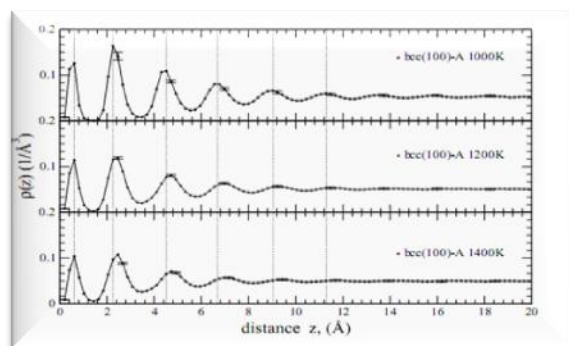

Figure 7. The diagram of density function for surfaces A of BCC solid based on distance at various temperatures.
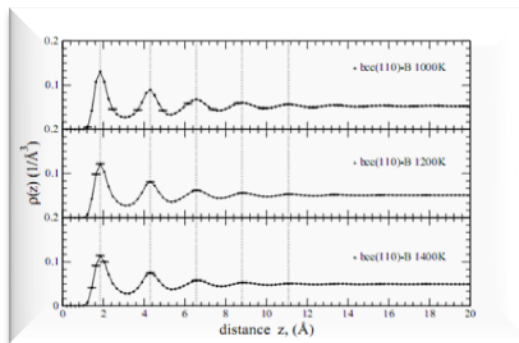

Figure 8. The diagram of density function for surfaces B of BCC solid based on distance at various temperatures.

4. Review and explanation

We have already explained the modified theory of the weighted density function and the attributes of solid BCC. On the other hand, we have investigated the interaction of solid and liquid states. By this way, we have shown how thermodynamic functions such as dependent energy and free energy change. Through this method, the density function has been attained upon the phase space. In addition, specific explanations regarding the mechanism of the interaction in a variety of solid states have been evaluated. Now, considering all the afore-mentioned details, it is time to conclude whatever we obtained and then we express the characteristics of the main model. Besides, we ought to present how our findings will convert into practical use. It is emphasized again that for the non-uniform classical fluid, the same approximation related to tough spherical molecules are assumed and typical correlation functions are used for the solid. Under this condition, even in the simplest case, we will be forced to do the calculation relevant to non-metallic sequences. Our computations have been done analytically with considering specific approximation. So, accurate and statistical calculations are postponed until another time. The approximation for the modified weighted function would be in the following form:

At the first step, the first *Brillouin* zone for the solid is considered. Apparently, in the equation, *N=8* and *r* is the same basic vectors in solid BCC network based on the below figure:
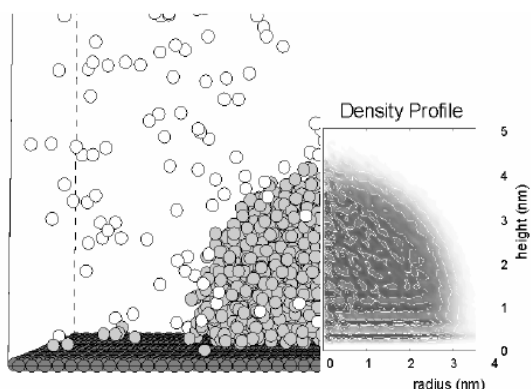
Figure 9. The schematic diagram the first stage liquid - solid BCC interaction

In this section, we consider the contact process of a liquid or solid substance with ease based on the approximations and findings in the previous chapters. As we know, realizing the sequence has numerous impacts on the phase changes on the contact cross-sections, the adhesion and superficial adhesion of fluid phase with solid and other vital parameters. In a similar process based on molecular approaches, it is possible to use these achievements so as to investigate the amount of liquid formed on the solid surface at the saturated vapors. In the same way, the difference between mechanical and thermodynamic methods and macroscopic ones is just in the determination of balance line related to three different phases of the substance. Through this method, the rate of heat transfer on contact surface could be obtained. But based on whatever we achieved, molecular dynamics methods are the best one to reach this goal and macroscopic simulation .

Figure 10. A view of the contact the liquid with the solid surface and its two-dimensional density profile in nanoscale.

The impact of potential on the interaction of the hitting liquid surface with solid has been indicated in figure 10. In the same way, potentials of the interaction NT till ε at the temperature of 100 degrees for six states have been presented on table 1.

Table 1. potential values of interaction εITN and contact angle at 100 degrees Celsius.

	$\varepsilon surf$	$\varepsilon INT \{10^{21}j\}$	$\theta[deg]$
E_o	0/73	0/228	___
E_1	1/29	0/404	135
E_2	1/86	0/581	110
E_3	2/43	0/758	79
E_4	2/99	0/935	49
E_5	3/56	1/112	___

It is witnessed that by increasing the amount of the potential interaction on surfaces, the adhesion of the liquid to solid surface rises. Furthermore, by possessing a strong potential interaction, separating the first surface of liquid, after hitting, is too difficult.
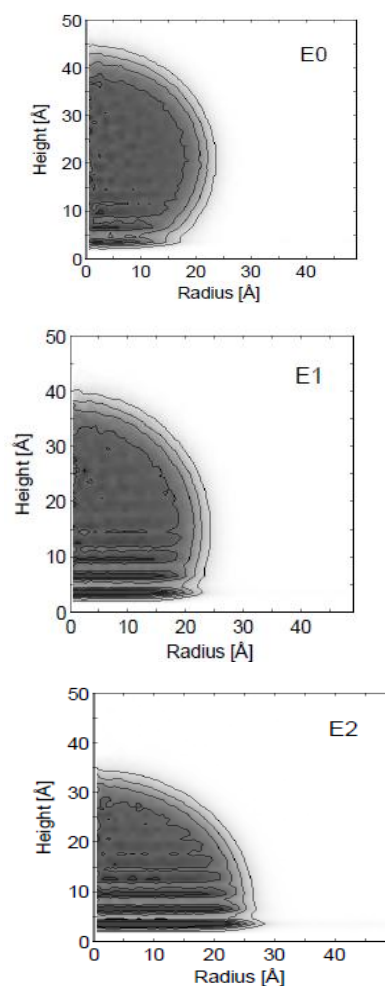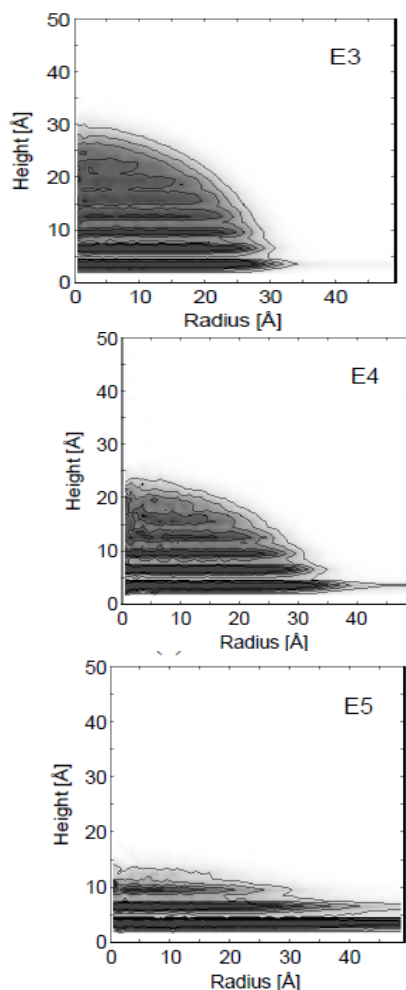
Figure 11. The two-dimensional density profile for *Lennard – Jones* potential

We note that The transformation always occurs in only one or two layers near the solid surface and the rest of the farther layers keep the same spherical shape. There is no need to explain how the hit angle is calculated. Thus, just its equation is obtained. By comparing the obtained values with the corresponding calculations relevant to various parameters in contact σINT in different states -such as on a single layer, surveying three consecutive layers, on a layer or stable molecules and etc- the effective potential is achieved as follows:

Where γ_{so} and γ_{sl} and γ_{lo} are the energy amongst three states of the balanced substance in order.

Now, it is time to focus on the contact between fluid with Platinum surface:
Platinum surface has been put vertically and the mirror boundary conditions on the top and periodic boundary circumstances are existed in all four directions. For Platinum surface, three layers of Identical molecules are considered. In various potential function, there is the first cross-section which each round of them is extracted from developing of spherical Henkel functions in biphasic distribution of contact surface.
Certainly, there is another potential function which we do not use and just introduce it.

Results and discussions

In this part, the usages of these outcomes are surveyed in color industry. As we obtained, one drop of a fluid stuck to the solid surface through a specific mechanism which is different due to the type of solid. Results present that the potential of the solid surface is more and the viscosity of the fluid increases, surface adhesion will be more. In the same way, based on the structure of a BCC solid, it is concluded that the surfaces (110) operate more efficiently than surfaces (100). By carrying out the experiment at a variety of temperatures and different substances, it could be noted that the temperature of the interaction environment impacts on the behavior of two surfaces. Eventually, the fusion and ingrowing values rises. Another vital point applied in industries is related to the temperature of the chamber which the solid is kept in should be nearly 20 degrees less than the temperature of the reaction flask after the interaction.
In practice, use of these outcomes requires simulating the corresponding process in experimental circumstances. It means that a model for the contact of the liquid -which might be epoxy resins or oil paints- should be designed with the BCC surface, moreover, its attributes are tested.

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