STUDIA UNIVERSITATIS BABES-BOLYAI, CHEMIA, LIV, 1, 2009

Dedicated to Professor Liviu Literat, at his 80th anniversary

MOLECULAR DYNAMICS SIMULATION OF THE HEAT TRANSFER BY NATURAL CONVECTION

SOARE GHEORGHE[a]

ABSTRACT. The heat transfer by natural convection between a surface of Cu (001) and water was studied with molecular dynamics simulation. A temperature gradient in a metal wall generates an electric charges gradient. On the cold face of the wall there are more electrons, as a result of the Thomson effect. On metal surface there are defects (dislocations, steps, terraces, kinks) and the electrons are not uniformly distributed. On the high defects there are more electrons than on the deep defects. From energetically point of view the metal surface is inhomogeneous. The molecules of the liquid are adsorbed on the metal surface and a small fraction of the molecular orbital overlaps on the orbital of the metal. The overlap allows the phonon exchange process between the adsorbed liquid molecules and the metal atoms. The proposed model takes into account both the process of metal surface reconstruction and the process of molecular cluster formation in liquid. The high defects are active centres which generate the movement of the liquid clusters over the metal surface. The results of the simulations show that the combination of these processes can gives a consistent prediction of the heat transfer coefficient by natural convection.

Keywords: *convection, heat transfer, modelling, molecular scale*

INTRODUCTION

It is an indubitable fact that flow and thermal phenomena can be only understood fundamentally by a molecular approach. Unfortunately, very few works were dedicated to study heat transfer mechanism through natural convection to molecular scale. A molecular model of the convection heat transfer mechanism is proposed in an anterior work [1], and a modality of calculation of the heat transfer efficiency in the molecular mechanism was analyzed in the work [2]. In an other work [3], the equilibrium of heat conduction in a very thin solid film, using molecular dynamics simulation with different boundary conditions, material, parameters and lattice configurations

[a] *Universitatea Politehnica din Bucureşti, Facultatea de Chimie Aplicată şi Ştiința Materialelor, Str. Polizu, Nr. 1, RO-011061 Bucureşti, Romania, g_soare@chim.upb.ro*

was studied. Many issues involved in the convection heat transfer are common and other scientific fields such as nano-tribology. Some of them are: adsorption of the molecules of lubricant on the solid surface and molecularly arrangement and flow of the lubricant in the boundary layer. More works were published in the area of the nanotribology [4-11]. In these works different aspects of the friction have been approached at molecular scale: static lubrication, dynamic lubrication, lubrication in boundary regime, the influence of molecule configuration, molecular rearrangements in a molecularly thin film between two solid surfaces during shear, etc.

In the present work a physical model and a mathematical model of convection heat transfer at molecular scale are proposed. The models take in consideration the elementary phenomena which take place on the solid fluid interface: adsorption, diffusion over surface, solid surface reconstruction and the transfer of the phonons to the adsorbed molecules of fluid. Molecular dynamics simulation helps to clarify some aspects of the convection mechanism.

RESULTS AND DISCUSSION

Physical model

To formulate physical model consider metal flat plate of Figure 1, in contact with two fluids (a hot fluid with temperature t_1 and a cold fluid with temperature t_2). The surfaces of the wall are heterogeneous in terms of energy. The heat transfers from hot fluid to cold fluid, in conformity with the molecular mechanism which was formulated by author in [1] and [2], and shown in Figure 1. An improved version of the physical model will be presented briefly below. The existence of a temperature gradient in direction of the solid wall thickness, ($t_{w1} > t_{w2}$), generates a gradient of density of the free electrons of metal (Thomson effect), so on the colder surface the density of the free electron N_2 is greater than the density of the electrons which are on the warmer surface, N_1.

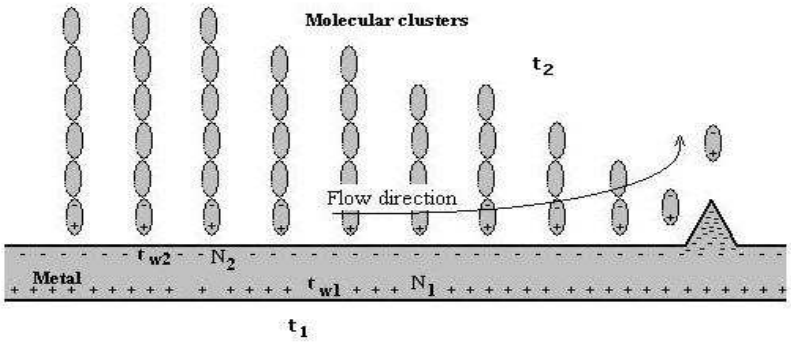

Figure 1. Physical model.

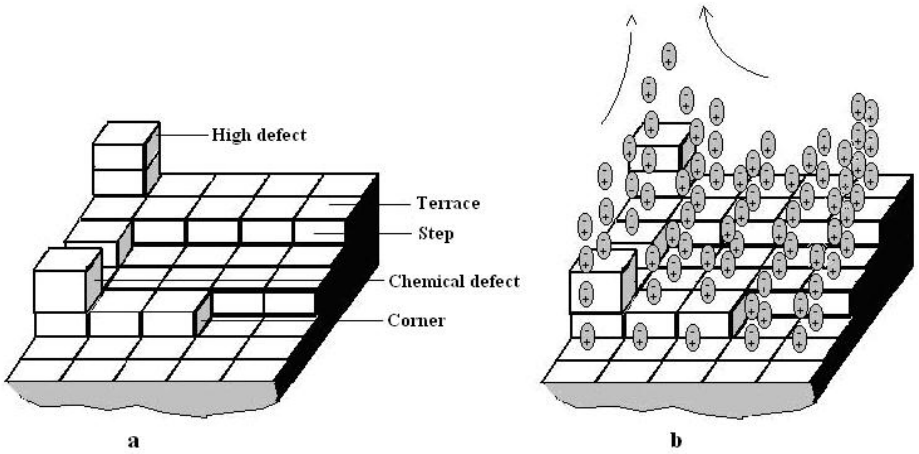

Figure 2. a) Possible defects of the solid surface. For simplicity, the atoms of the solids were represented as a parallelepiped,
b) Molecular multilayer adsorbed on the surface. The two arrows indicate the flow of the molecules and clusters of molecules.

The cold face is loaded with negative electrical charges and the hot face remains positively charged. Free electrons can not be spread evenly on the surface of the metal because the surface is not a perfect plane. Because of surface defects (dislocations, terraces, stairs, corners), see Figures 1 and 2, these electrons are preferentially distributed on the surface. On the high defects the electron density is greater than the electron density on both deep defects and the terraces which exist on the metal surface. For this reason, on the high defects is a greater intensity of the electric field which is generated by these electric charges. The molecules of liquid are adsorbed on the metal surface. Adsorbed molecules move over the surface and capture phonons from the crystalline metal. The movement is a result of the following forces action:

- the forces of attraction and repulsion between molecules in fluid;
- the forces of attraction and repulsion between the molecule of the fluid and solid;
- the forces of attraction and repulsion between the adsorbed molecule and nearest high defects, where the electric field is more intense.

Movement of the adsorbed molecules is directed towards nearest high defect, which becomes an active centre that generates natural convection.

Migration of the molecules over the surface, under the action of the above-mentioned forces, intensifies the emission of the phonons. Permanent dipoles molecules can migrate more quickly than originally non polar molecules. But a non polar molecule becomes a polar one as a result of an

inductive polarization process. In accordance with the mechanism proposed in this theory, the process of heat transfer by natural convection implies: adsorption, polarization and an induced movement towards the active centres of the solid surface, the phonons capture and expulsion of molecules outside the solid-fluid interface.

Effectiveness of the phonons absorption process

The absorption of the phonons is conditioned by adsorption of liquid molecules on the solid surface, and it involves formation of bounds between the fluid molecules and metal atoms. These bounds imply overlapping of atomic and molecular orbital. If the overlapping degree is higher, the capture of the phonon is more efficient, meaning that will increase the quantity of transferred energy. Also, the overlapping of the orbital allows an exchange of electrons between the molecules and atoms of metal, which means an energy exchange process.
In this work we consider that the degree of overlapping orbital is, in conformity with [2]:

$$\eta = \frac{EB_{ms}}{E_{ms}} \tag{1}$$

where:

$$EB_{ms} = \frac{E_{m-m}}{2} + E_s^0\ (1 - C_F\ ) + \gamma_P\ (\chi_m\ - WF_s\ )^2 \tag{2}$$

In which:

$$C_F\ = 2\ (1 - \frac{V_s}{N_A}\ )$$

$$E_{ms} = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{3}$$

In equations (1 – 3) EB_{ms} is the energy of a hypothetical chemical bond of molecule with solid surface [12], E_{ms} is the Lennard-Jones (LJ) 12-6 potential energy between molecule and solid surface, E_{m-m} is molecule-molecule bond energy, E^o_S – electron energy on surface, N_A - a constant, WF_S - work function of the metal surface (energy), r - current distance surface-molecule, Vs - valence of the solid, γ_P – a constant, χ - electronegativity, ε – LJ energy parameter, σ - LJ length parameter.

Solid surface reconstruction

The reconstruction of the surface of the metal should be understood as a change in topography of the surface, imposed by the forces which act

on the solid-fluid interface during the convection heat transfer [13]. Under the action of such forces, deep defects and high defects are continuing to appear on the solid surface. The probability with which an atom of a crystal forms a high defect is given by Boltzmann factor:

$$P = e^{-\frac{E_d}{K_B T}} \tag{4}$$

In which: E_d is the energy of displacement of a particle, K_B - Boltzmann constant, T - absolute temperature.

If there are N_S atoms per unit area of solid, the number n_S of defects is:

$$\frac{n_S}{N_S - n_S} = e^{-\frac{E_S}{K_B T}} \tag{5}$$

But n_S is much smaller than N_S and then we can write:

$$n_S = N_S e^{-\frac{E_S}{K_B T}} \tag{6}$$

The high defects appear together with the Schottky defects too, by bringing of an atom from the crystal at surface. The number of these defects, in a similar way, is expressed as follows:

$$n_V = N_V e^{-\frac{E_V}{K_B T}} \tag{7}$$

In which: E_V is the energy necessary to transport an atom from inside of the crystal to the surface, and N_V - the number of atoms inside unit volume per unit surface. The total number of high defects on the solid surface, in thermal equilibrium, is:

$$n_T = n_S + n_V \tag{8}$$

Mathematical model

On the base of the physical model, presented above, was formulated the mathematical model, taking into account all this elementary processes and the assumptions which follow:

- the temperature of the surface of the wall is constant;
- in solid, the transversal acoustic phonons are only considered;
- the attractive and repulsive forces, presented above, are electrostatic in nature.

Mathematical model is formed, mainly, from equations (1-11).

The convection heat transfer coefficient is expressed in the classical way:

$$\alpha = \frac{Q}{A\left(t_w - t_f\right)} \tag{9}$$

In equation (9), A is the heat transfer area, Q – heat flow rate, t_w – temperature of the surface of the wall, and t_f - fluid temperature.

The heat flow rate is the energy of the absorbed phonons in the interval of time in which the molecules are adsorbed on the solid surface. The energy of a phonon is:

$$\varepsilon = h\upsilon \tag{10}$$

In which: h is Plank constant and υ - phonon frequency.

The time in which the molecules of fluid are adsorbed on the surface is calculated with velocity of the molecules. The velocity is a result of the forces which act on the molecules [3].

The coverage degree x_a of metal surfaces by adsorption molecules of liquid has been calculated with a specific equation [17]:

$$x_a = \frac{k_0}{\sqrt{T}} \exp\left(\frac{E_a}{K_B T}\right) \tag{11}$$

In which: k_0 is a constant, T - absolute temperature and E_a – adsorption energy.

The equation includes the influence of temperature, so that coverage of the surface with adsorbed molecules of liquid is a function of both the temperature and the topology of the surface of the wall.

The basis of the calculations

In order to calculate the convection heat transfer coefficient it was considered the surface of copper Cu (001), a face-centered-cubic metal. On this surface high defects are placed in the four tips of a square. In our simulations, we considered that all high defects are in the same form and contain the same number of atoms, namely 50 atoms in a conical arrangement with four layers. The surface of the copper is in a process of restructuring and the number of defects is a function of temperature, as equations (6) and (7) show, and the topological data of the surface are in a continuous change when temperature changes. The defects can diffuse over copper surface [14]. Rising of the temperature leads to rising of the number of defects, but the form and dimensions of the defects are conserved. It was not taken into account reduction in the number of defects (active centres) by the phenomenon of self-coalescence. In order to calculate the force which acts on the clusters we considered the closest 25 active centres around a cluster. The molecules of liquid form cluster with variables size. The energy of the clusters was calculated with a Lennard-Jones

potential, and the energy of adsorption metal-cluster was calculated with a Lennard-Jones potential too, [6] and [15]. The number of molecules in an adsorbed cluster on the surface decreases because of the shear stress that appears during of the flowing. In the dynamic simulation of their diffusion, the liquid clusters have a rectilinear trajectory and the velocity is a function of time.

Results of simulations

The convection heat transfer coefficient was calculated with an own computer program of calculation, based on the mathematical model described above, and using MATLAB programming language. The heat transfer process by natural convection from the surface of Cu (001) to water was simulated. Calculus of the convection heat transfer coefficient was made in the assumption that water forms linear clusters with 6 molecules (hexamers), which are oriented perpendicularly to the surface of heat transfer. Figure 3 shows the convection heat transfer coefficient as a function of difference between the solid temperature and the liquid temperature. Values obtained with the classical equations (12, 13) [16], and those obtained with the proposed model are in good harmony.

$$Nu = 0.54\left(Gr\,\mathrm{Pr}\right)^{1/4} \quad for\ 10^4 < Gr\,\mathrm{Pr} < 10^7 \tag{12}$$

$$Nu = 0.15\left(Gr\,\mathrm{Pr}\right)^{1/3} \quad for\ \ Gr\,\mathrm{Pr} > 10^7 \tag{13}$$

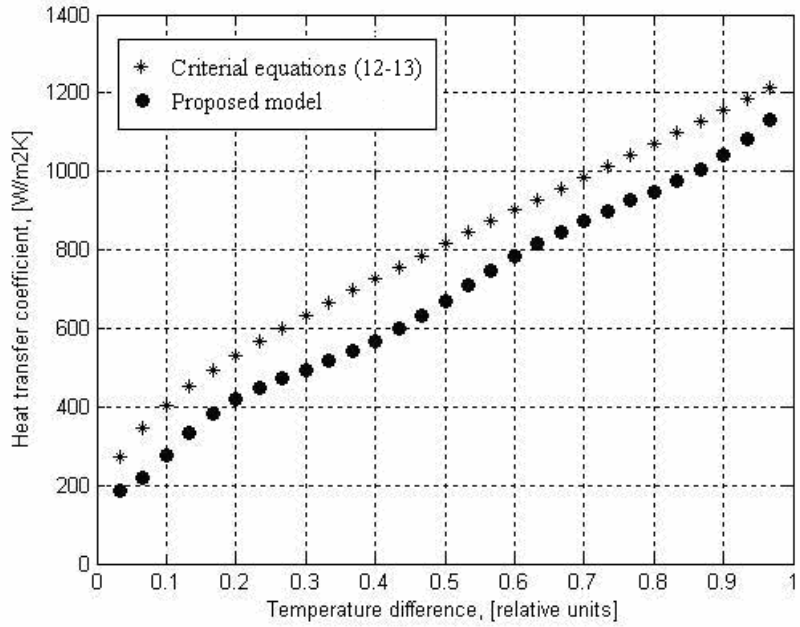

Figure 3. Heat transfer coefficient by natural convection in the system water / Cu (001).

The sinuosity of the curve obtained with the proposed model in this work is due to the phenomenon of surface reconstruction and is frequently observed in experimental measurements.

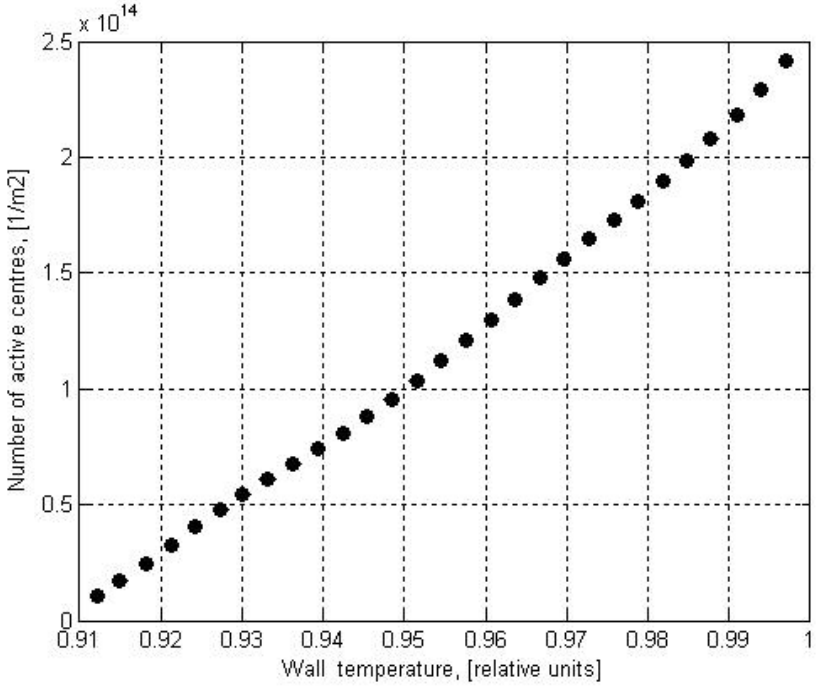

Figure 4. The restructuring of the copper surface quantitatively expressed by the number of active centres involved in the convection heat transfer.

As noted above, surface reconstruction is the modification of copper surface topology as a result of the copper atoms diffusion to the surface. Increasing of the metal temperature leads to increasing of the number of high defects, which are in fact cluster of atoms of copper. The result of the copper surface restructuring simulation is quantitatively expressed by the number of active centres involved in the convection heat transfer. Figure 4 shows this phenomenon.

But, increasing the number of active centres increase intensity of heat transfer process by natural convection, Figure 5.

Through the phenomenon of surface reconstruction, the natural convection mechanism is similar to the mechanism of heat transfer in boiling. The intensity of the heat transfer in boiling increases with the difference temperature because the number of nucleation centres increases.

Another issue considered is that of changing the thickness of adsorbed molecular layer, flowing on the surface solid. In the process of heat transfer, the thickness of the adsorbed fluid multilayer does not remain constant.

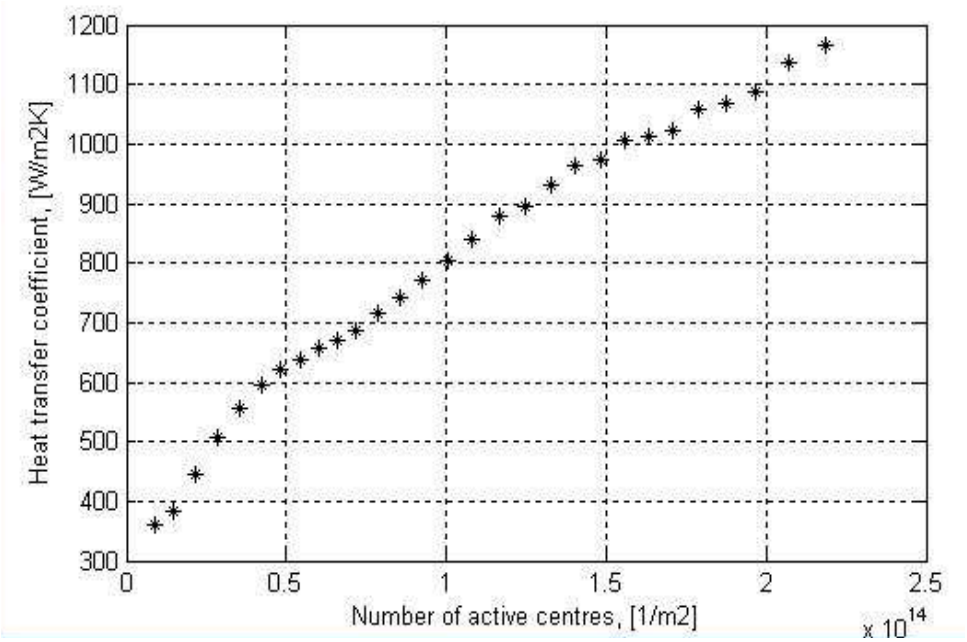

Figure 5. Reconstruction of the surface affects intensity of the natural convection.

We considered that water molecular clusters initially consist in six molecules linearly arranged. The thickness of this layer of molecules varies due the impulse transfer process, which implies a shear stress. Figure 6 shows this change in thickness of the layer, for a difference between the temperature of the wall and the temperature of the water of 5K.

The heat transfer coefficient data, presented above in Figure 3, were obtained, taking account changing in the thickness of the layer of water molecules adsorbed in the form of cluster. Results of simulations show that cluster mass strongly influences the convection heat transfer coefficient, i.e. increases with decreasing of the cluster's mass.

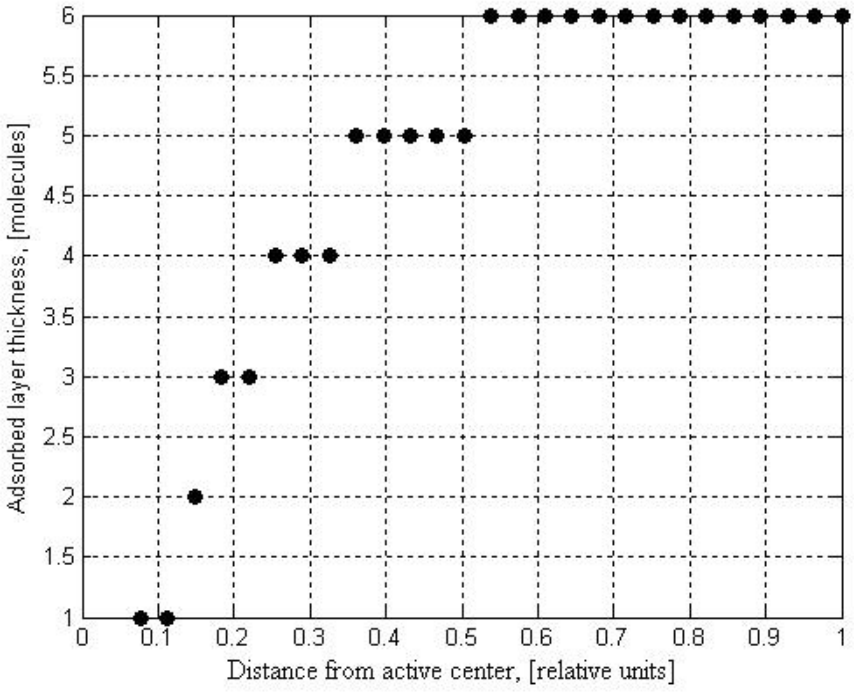

Figure 6. Changing the thickness of the water multilayer during of the convection heat transfer.

This change in thickness of the multimolecular layer is similar to that of reducing the hydrodynamic boundary layer, known from boundary layer theory, when the flow changes from laminar regime to turbulent regime.

CONCLUSIONS

A physical and a mathematical model of convection heat transfer, at molecular scale, were formulated.

Using molecular dynamics method and with an own computer program, the convection heat transfer and the surface reconstruction of the Cu (001) were simulated. The convection system which was investigated is water on Cu (001). The mass and dimensions of the molecular clusters largely affect the rate of heat transfer. If the mass decreases, the convection heat transfer coefficient increases.

The phenomenon of surface reconstruction, its influence on the intensity of convection heat transfer process, and continuously changing of the boundary layer thickness were outlined quantitatively.

Simulation of the process at molecular scale emphasizes the conclusion that between the mechanism of natural convection and the mechanism of heat transfer in boiling there is an obvious similarity.

The results of the simulations show that combining all these processes we can give a consistent prediction of the heat transfer coefficient by natural convection.

Proposed model is a more realistic image of the process of natural convection than the boundary layer theory.

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