

## BINARY LIQUID MODEL

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August 22, 2011 / LBM Workshop

# OUTLINE

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## BINARY LIQUID MODELS

As we discussed before one wants to introduce the model which avoids the condensation and evaporation of species, basically it's many component one phase models, so-called binary-liquid model. The main model is density-matched binary liquid model.

## EQUATIONS DERIVATION:

Suppose two fluids ( $A$  and  $B$  components) having densities  $\rho_A$  and  $\rho_B$ . We introduce the volume fraction  $C$  ( $0 < C < 1$ ) of component  $A$ . Then the densities can be calculated as:

$$\begin{aligned}\tilde{\rho}_A &= C\rho_A; \quad \tilde{\rho}_B = (1 - C)\rho_B \\ \rho &= C\rho_A + (1 - C)\rho_B\end{aligned}$$

We start with the conservation of mass of the species  $A$ :

$$\partial_t \tilde{\rho}_A + \nabla \cdot \mathbf{n}_A = 0,$$

where the flux  $\mathbf{n}_A = \tilde{\rho}_A \mathbf{u} - \rho_A \mathbf{j}_A$ , where  $\mathbf{u}$  is the overall fluid velocity to be defined later and  $\mathbf{j}_A$  is the volume diffusion flux between two fluids. Therefore the conservation equation becomes:

$$\partial_t \tilde{\rho}_A + \nabla \cdot (\tilde{\rho}_A \mathbf{u}) - \nabla \cdot (\rho_A \mathbf{j}_A) = 0$$

If we write in terms of volume fraction one can obtain the following equations for species  $A$  and  $B$ :

$$\begin{aligned}\partial_t C + \nabla \cdot (\mathbf{u}C) - \nabla \cdot \mathbf{j}_A &= 0 \\ \partial_t (1 - C) + \nabla \cdot [(1 - C)\mathbf{u}] - \nabla \cdot \mathbf{j}_B &= 0\end{aligned}$$

## MACROSCOPIC EQUATIONS

From these two equations by summing up and minusing it one can obtain the following two fundamental equations:

$$\begin{aligned}\partial_t \rho + \nabla \rho \cdot \mathbf{u} &= \nabla \cdot (\rho_A \mathbf{j}_A + \rho_B \mathbf{j}_B) \\ \nabla \cdot \mathbf{u} &= \nabla \cdot (\mathbf{j}_A + \mathbf{j}_B)\end{aligned}$$

When we assume that the liquid is incompressible - does it mean that mass fluxes or volumetric fluxes are of different signs?

Incompressibility requires the conservation of the volumetric fluxes. In terms of equations it can be rewritten as follows:

$$\begin{aligned}\mathbf{j}_A &= -\mathbf{j}_B = \mathbf{j} \\ \nabla \cdot \mathbf{u} &= 0 \\ \partial_t \rho + \nabla \cdot (\rho \mathbf{u}) - (\rho_A - \rho_B) \nabla \cdot \mathbf{j} &= 0\end{aligned}$$

To avoid any misunderstanding we further concentrate on the case of the binary liquids, i.e.  $\rho_A = \rho_B$ . In this case mass and volumetric fluxes coincide with each other, i.e.  $\rho_A \mathbf{j}_A = \rho_B \mathbf{j}_B$  and  $\mathbf{j}_A = \mathbf{j}_B$ .

## MACROSCOPIC EQUATIONS

Adding another equation to the system (Navier-Stokes equation) one can obtain the following system of equations describing the incompressible binary-liquid model:

$$\nabla \cdot \mathbf{u} = 0$$

$$\partial_t C + \mathbf{u} \cdot \nabla C - \nabla \cdot \mathbf{j} = 0$$

$$\rho(\partial_t \mathbf{u} + \mathbf{u} \cdot \nabla \mathbf{u}) = -\nabla p + \nabla \cdot [\eta(\nabla \mathbf{u} + \nabla \mathbf{u}^T)] + \mathbf{F}$$

Still we don't know the form of the volumetric flux  $\mathbf{j}$  and the form of the force  $\mathbf{F}$ . The continuous interface theory by van der Waals can help us to see the form of necessary terms.

### VAN DER WAALS

“We can invert the principle of equilibrium as follows: A given amount of matter distributes itself in a given space in such a way that, for a given value of the total entropy, the total energy has a minimum, or  $\delta \int \rho \epsilon dV = 0$  with the subject of the following conditions: mass  $\int \rho dV = \text{const}$  and entropy  $\int \rho s dV = \text{const}$ .”

## FREE ENERGY

Following the calculus variation one can put the condition of constant entropy inside the minimizing functional:

$$\delta \int \rho(\epsilon - \lambda s) dV = 0, \delta \int \rho \psi dV = 0$$

where coefficient  $\lambda$  can be shown to be temperature  $T$ . Therefore, the minimization is done for the Helmholtz free energy functional,  $H = U - TS$ . From the calculus of the variation one can put the condition of the conserved mass in the system ( $\int \rho dV = const$ ) to the integral expression, introducing a Lagrange multiplier  $\mu$ :

$$\delta \int \rho(\psi - \mu) dV = 0$$

At this particular moment, as far as we are introducing the binary-liquid model one needs to make an assumption of the free energy functional to be a function of phase parameter  $\phi$  (which is the same as  $C$  except it spans not from 0 to 1, but from  $-1$  to  $1$  for symmetry reasons) and density  $\rho$ , i.e.  $\psi = \psi(\rho, \phi, \phi')$ . However, the variation occurs by the function  $\phi$  as far as we are interested mainly in the phase order parameter. Saying that the coefficient  $\mu$  (chemical potential) can be expressed as follows:

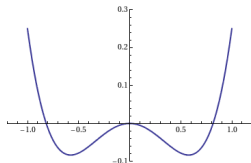
$$\mu = \frac{\delta \rho \psi}{\delta \phi} = \partial_{\phi} \rho \psi - \nabla \cdot \partial_{\nabla \phi} \rho \psi$$

## DOUBLE WELL POTENTIAL

The chemical potential needs to be a constant across the interface. But still we don't know the form of the free-energy functional. One can show (see the thesis of van der Waals) that the excess of the free energy can be taken as double well potential with the inclusion of the surface tension:

$$\mathcal{F} = \int \left( -\frac{A}{2}\phi^2 + \frac{A}{4}\phi^4 dV + \frac{k}{2}(\partial_\alpha\phi)^2 + \frac{\rho \ln \rho}{3} \right) dV,$$

where the double well potential is responsible for phase separation and stability of the phase separation. Term  $\frac{\rho \ln \rho}{3}$  stays for the equation of state  $p_0 = \frac{\rho}{3}$





## CHEMICAL POTENTIALS AND PRESSURE TENSOR

Therefore, one can express the value of the volumetric chemical potential coming from Lagrange-Euler minimization functional equation

$\partial_\phi \mathcal{F} - \partial_\alpha \partial_\alpha \partial \partial_\alpha \phi L$ :

$$\mu = A(-\phi + \phi^3) - k\Delta\phi.$$

Variational calculus as well state that there is the conservation law which is in our case the momentum flux modification:

$$\partial_\beta P_{\alpha\beta} = \phi \partial_\alpha \mu$$

$$P_{\alpha\beta} = \left( \frac{\rho}{3} - A\phi^2 + \frac{3}{4}\phi^4 + k\phi\Delta\phi + \frac{k}{2}|\nabla\phi|^2 \right) \delta_{\alpha\beta} + k\partial_\alpha\phi\partial_\beta\phi$$

That is the most crucial result from the binary liquid theory. In the system for the binary liquids we already defined  $\mathbf{F} = -\phi\nabla\mu$  which modifies the equation of state. However one still needs to give the expression for  $\mathbf{j}$ , which is of course proportional to  $\nabla\mu$  because of the thermodynamical definition of chemical potential  $\mu = \frac{\partial U}{\partial N}$ , stating for the energy change if the number of particles is changed. We state  $\mathbf{j} = M\nabla\mu$ , where  $M$  is the mobility.

## SYSTEM OF EQUATIONS FOR THE BINARY LIQUID MODEL

Therefore one needs to solve the following equations:

$$\nabla \cdot \mathbf{u} = 0$$

$$\partial_t \phi + \mathbf{u} \cdot \nabla \phi = \nabla \cdot M \nabla \mu$$

$$\rho(\partial_t \mathbf{u} + \mathbf{u} \cdot \nabla \mathbf{u}) = -\nabla p + \nabla \cdot [\eta(\nabla \mathbf{u} + \nabla \mathbf{u}^T)] + \phi \nabla \mu,$$

where the force modifies the equation of state. Other parameters are defined as follows:

- Surface tension is  $\sigma = \sqrt{\frac{8 k A}{9}}$
- The interface width (to be shown later)  $\xi = 2\sqrt{2}\sqrt{\frac{k}{A}}$
- Mobility coefficient  $M$  is usually chosen as the function of  $\phi$ , i.e.  
$$M(\phi) = \frac{(\phi-1)(\phi+1)}{4}.$$

## BOUNDARY CONDITIONS

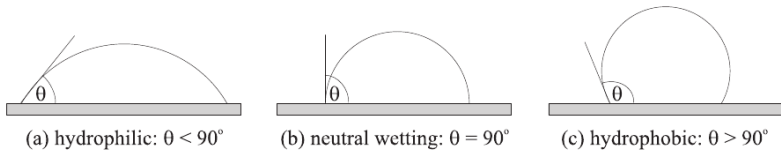
The boundary conditions in the framework of the free energy approach are simple: one needs to specify the normal gradient of the phase on the wall:

$$h = k\partial_{\perp}\phi$$

For example for the case of the droplet on the surface the contact angle (courtesy of H. Kusumaatmaja) is defined through the factor  $h$  as:

$$h = \sqrt{2kA} \operatorname{sign}\left(\frac{\pi}{2} - \theta\right) \sqrt{\cos\left(\frac{\alpha}{3}\right) \left(1 - \cos\left(\frac{\alpha}{3}\right)\right)},$$

where  $\alpha = \cos^{-1}(\sin^2 \theta)$



# LATTICE BOLTZMANN IMPLEMENTATION

For the lattice Boltzmann system which corresponds to the slightly compressible case one needs to resolve the following system of equations:

$$\partial_t \rho + \partial_\alpha \rho u_\alpha = 0$$

$$\partial_t \rho u_\alpha + \nabla \cdot \rho u_\alpha u_\beta = -\nabla \frac{\rho}{3} + \nu \partial_\beta (\rho \partial_\beta u_\alpha + \rho \partial_\alpha u_\beta) + \phi \nabla \mu$$

$$\partial_t \phi + \partial_\alpha \phi u_\alpha = M \Delta \mu,$$

where we assume a few important things:

- Mobility  $M$  is the constant coefficient but not a function.
- The model is slightly compressible - the velocity field is not divergent-free.

One can notice that to solve the system above one needs two sets of the distribution functions  $f_i$  and  $g_i$ . In what follows we will thoroughly describe the LBM implementation.

# LATTICE BOLTZMANN IMPLEMENTATION

Therefore the lattice Boltzmann implementation consists from the following steps:

- 1 Initialize fields. Density can be taken everywhere as 1. The phase needs to be initialized as  $-1$  for assumed gas locations and  $1$  for assumed liquid locations.
- 2 Calculate macroscopic parameters  $\phi = \sum_i g_i$  and  $\rho = \sum_i f_i$ . Calculate velocities  $\rho \mathbf{u} = \sum_i f_i \mathbf{c}_i$ . Notice that velocity is calculated from the density probability distribution function.
- 3 Calculate necessary laplacians  $\Delta$  and gradients  $\nabla$  for the phase field
- 4 If the external force is specified then shift the equilibrium velocity as  $\rho \mathbf{u}^{eq} = \sum_i f_i \mathbf{c}_i + \frac{\mathbf{F}}{2} = \rho \mathbf{u} + \frac{\mathbf{F}}{2}$
- 5 Calculate equilibrium functions (to be specified later). Notice that the velocity is the same for the density and phase distribution functions.

## LBM IMPLEMENTATION: CONTINUE

- 6 Perform collision for fluid nodes:
- Notice that the binary liquid model can simulate liquids with different viscosities. The viscosity is controlled by two relaxation parameters  $\tau_{gas}$  and  $\tau_{liq}$ . The relaxation rate for fluid node is calculated based on phase (usually is linear function):  $\tau_\rho = \tau_{gas} + \frac{\phi+1}{2}(\tau_{liq} - \tau_{gas})$
  - Collision perform two collisions for the hydro field and phase field ( $\omega_\rho = \frac{1}{\tau_\rho}$  and  $\omega_\phi = \frac{1}{\tau_\phi}$ ):

$$f_i^* = f_i(1 - \omega_\rho) + \omega_\rho f_i^{eq} + F_i; g_i^* = g_i(1 - \omega_\phi) + \omega_\phi g_i^{eq}$$

- 7 Perform BB and other boundary conditions
- 8 Perform streaming to the fluid domain.
- 9 Loop

## PHASE EQUILIBRIUM FUNCTIONS

For phase we are simulating the following equation:

$$\partial_t \phi + \partial_\alpha \phi u_\alpha = M \Delta \mu,$$

where  $\mu = A(-\phi + \phi^3) - k\Delta\phi$ . We are solving non-linear equation, then the equilibrium functions will have another form in comparison with the already defined before. Overall, the equilibrium phase distribution function will have the following form (we present it here for  $D2Q9$  model):

$$g_i = w_i \left( 3\Gamma\mu + \phi 3u_\alpha c_{i\alpha} + \phi (c_{i\alpha} c_{i\beta} - \frac{1}{3}) \right), \text{ for } 1 \leq i \leq 8, g_0 = \phi - \sum_{i=1}^8 g_i,$$

where the chemical potential  $\mu$  is calculated before, and velocity  $\mathbf{u}$  is supplied before as well. It can be shown that the mobility parameter  $M = \frac{1}{3}(\tau_\phi - \frac{1}{2})\Gamma$ . Weights are as usual weights defined before

$$w_i = \left( \frac{4}{9}, \frac{1}{9}, \frac{1}{9}, \frac{1}{9}, \frac{1}{9}, \frac{1}{36}, \frac{1}{36}, \frac{1}{36}, \frac{1}{36} \right).$$

## TWO APPROACHES

In comparison with the phase distribution functions there are two approaches for density equilibrium distribution functions:

- 1 Simulation through the force:

$$\mathbf{F} = -\phi \nabla \mu$$

In this case one can use the usual equilibrium for density as:

$$f_i^{eq} = w_i \rho \left( 1 + 3c_{i\alpha} u_\alpha^{eq} + \frac{9}{2} (c_{i\alpha} c_{i\beta} - \frac{1}{3}) u_\alpha^{eq} u_\beta^{eq} \right)$$

$$\rho \mathbf{u}^{eq} = \sum_i f_i \mathbf{c}_i + \frac{\mathbf{F}}{2}$$

$$\mathbf{F} = -\phi \nabla \mu$$

The collision operator is  $f_i^* = f_i(1 - \omega_\rho) + \omega_\rho f_i^{eq}$  and the force population is by Guo formulation

$$F_i = w_i \left( 1 - \frac{\omega_\rho}{2} \right) (3(\mathbf{c}_i - \mathbf{u}) + 9(\mathbf{c}_i \cdot \mathbf{u}) \mathbf{c}_i) \cdot \mathbf{F}.$$



## SECOND APPROACH

- ② The second approach (more spread) is to include forcing into the equilibrium distribution function:

$$f_i^{eq} = w_i \rho \left( 3 \left( \frac{\rho}{3} + A \left( -\frac{\phi^2}{2} + \frac{3}{4} \phi^4 \right) - k \phi \Delta \phi \right) + 3 c_{i\alpha} u_\alpha^{eq} \right. \\ \left. + \frac{9}{2} \left( c_{i\alpha} c_{i\beta} - \frac{1}{3} \right) u_\alpha^{eq} u_\beta^{eq} \right) + k \left( w_i^{xx} (\partial_x \phi)^2 + w_i^{yy} (\partial_y \phi)^2 \right. \\ \left. + w_i^{xy} \partial_x \phi \partial_y \phi \right), \text{ for } 1 \leq i \leq 8$$

$$f_0^{eq} = \rho - \sum_{i=1}^8 f_i^{eq}$$

where additional weights  $w_i^{xx}$ ,  $w_i^{xy}$  and  $w_i^{yy}$  are responsible for the distribution of the forcing through all equilibrium functions:

$$w_i^{xx} = \left\{ 0, \frac{1}{3}, -\frac{1}{6}, \frac{1}{3}, -\frac{1}{6}, -\frac{1}{24}, -\frac{1}{24}, -\frac{1}{24}, -\frac{1}{24} \right\}$$

$$w_i^{yy} = \left\{ 0, -\frac{1}{6}, \frac{1}{3}, -\frac{1}{6}, \frac{1}{3}, -\frac{1}{24}, -\frac{1}{24}, -\frac{1}{24}, -\frac{1}{24} \right\}$$

$$w_i^{xy} = \left\{ 0, 0, 0, 0, 0, \frac{1}{4}, -\frac{1}{4}, \frac{1}{4}, -\frac{1}{4} \right\}$$

## NUMERICAL STENCILS

The last thing to finalize the lattice Boltzmann implementation for the binary liquid model is to specify the numerical stencils for laplacian delta and gradients  $\partial_x$  and  $\partial_y$ :

$$\Delta = \begin{bmatrix} \frac{1}{6} & \frac{4}{6} & \frac{1}{6} \\ \frac{4}{6} & -\frac{20}{6} & \frac{4}{6} \\ \frac{1}{6} & \frac{4}{6} & \frac{1}{6} \end{bmatrix}; \quad \partial_x = \begin{bmatrix} -\frac{1}{12} & 0 & \frac{1}{12} \\ -\frac{4}{12} & 0 & \frac{4}{12} \\ -\frac{1}{12} & 0 & \frac{1}{12} \end{bmatrix}; \quad \partial_y = \begin{bmatrix} \frac{1}{12} & \frac{4}{12} & \frac{1}{12} \\ 0 & 0 & 0 \\ -\frac{1}{12} & -\frac{4}{12} & -\frac{1}{12} \end{bmatrix}$$

## FEATURES AND PARAMETERS

There are a number of good features to work with the binary-liquid model:

- The model is thermodynamically consistent and physical. The only problem is the uniform density which you need to consider.
- The interface usually occupies 3 – 5 lattice nodes.
- Good for contact angle simulations.
- No additional condensation and evaporation.
- Explicitly given surface tension  $\sigma = \frac{8kA}{9}$ .

One needs as well know some parameters to start with. Usually a good set of parameters is  $\Gamma = 1$ ,  $\tau_\phi = 1$ ,  $k = 0.04$ ,  $A = 0.04$ ,  $\tau_{gas} = 0.7$  and  $\tau_{liq} = 2.5$ . This set of parameters gives the interface thickness around 5 lattice units and gas-liquid viscosity ratio  $\frac{\mu_{liq}}{\mu_{gas}} = 10$ .

## BE AWARE

A few things to know from the numerical point of view:

- If one needs to adjust the surface tension which equals to  $\sigma = \sqrt{\frac{8kA}{9}}$  then the suggestion is to scale your parameters as  $k \propto A$ , because this choice will conserve the interface thickness  $\xi = 2\sqrt{2}\sqrt{\frac{k}{A}}$ .
- If one needs to increase the gas-liquid viscosity ratio  $\frac{\mu_{liq}}{\mu_{gas}}$ , then it can be done either with increase of  $\tau_{liq}$  or the decrease of  $\tau_{gas}$ . The increase in  $\tau_{liq}$  produces the inaccuracies, since the BGK scheme accuracy is proportional to  $\left(\tau - \frac{1}{2}\right)^2$ . In this case the simulation with TRT/MRT can help. The decrease in  $\tau_{gas}$  results in stability issues, since  $\tau_{gas}$  is close to stability limits  $\frac{1}{2}$ . In this case one needs to increase  $\Gamma$  for the interface to keep up with low viscosity. Increase of  $\Gamma$  results in the decrease of available parameters  $A$  and  $k$ . Therefore, one needs to search for the compromise. However, recent studies show that TRT/MRT models can help as well.