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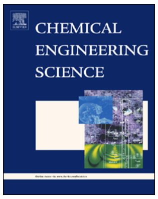

Modeling with statistical hydrodynamic quantities of mass transfer across gas–liquid interface with Rayleigh convection

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HIGHLIGHTS

- Interfacial Rayleigh convection is considered as a special turbulent flow.
- Mass transfer in Rayleigh convection is highly dependent upon the hydrodynamics.
- Mass transfer process modeling for Rayleigh convection is accomplished.
- The relation of hydrodynamic to mass transfer is interpreted by the field synergy.

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ABSTRACT

The process of CO_2 absorption into a horizontal liquid layer was simulated with the hybrid Lattice-Boltzmann/finite-difference method (LBM–FDM). The simulation results showed that as the absorption process progressed, Rayleigh convection was generated by the concentration gradient near the interface. The formation of a complex flow pattern was accompanied by a mass transfer mechanism transformation, i.e., from molecular diffusion to a combination of diffusion and convection. This study attempted to introduce the hydrodynamic parameters, such as ε, surface divergence, and so on, that the turbulent mass transfer models had used to predict k_t in Rayleigh convection and, moreover, revealed the inherent relationship between hydrodynamics and mass transfer from the viewpoint of field synergy. The computed results indicated that the surface divergence model accurately predicts k_t in magnitude with a phase difference. By further analysis, the low synergy degree between the velocity vector and concentration gradient is clarified.

1. Introduction

Mass transfer across an interface may lead to the instabilities in the near-surface region due to the concentration gradient. This is referred to as Rayleigh convection in the literature and can be characterized by the dimensionless Rayleigh number (Bénard, 1901; Rayleigh, 1916). Rayleigh convection is expected only if the mass transfer occurs in a so-called Rayleigh-unstable system with a positive Rayleigh number. Researchers have been attracted by this phenomenon because it can enhance mass/heat transfer in many engineering applications (Orell and Westwater, 1962; Proctor et al., 1998; Sun et al., 2002; Arendt et al., 2004; Farajzadeh et al., 2009). Previous reports in the literature concerning Rayleigh convection mainly focused on the optical observation of interfacial convection structures (Arendt et al., 2004; Thomas and Nicholl, 1967; Blair and Quinn, 1969; Okhotsimskii and Hozawa, 1998; Kutepov et al., 2001), the theoretical prediction of the onset time of interfacial convection (Riaz et al., 2006; Kim et al., 2006; Tan and Thorpe, 1999; Sun and Fahmy, 2006; Sun, 2012), and the quantitative measurement of mass transfer rate with interfacial convection. Sun et al. (2002), Burger et al. (1974), and Hozawa et al. (1984) experimentally studied the mass transfer rate of gas–liquid absorption in various mass transfer process. From their works (e.g., Sun et al., 2002, Figs. 10, 11 13, and 14; Burger et al., 1974, Fig. 5; Hozawa et al., 1984, Figs. 10, 11 13, and 14), it can be determined that the mass transfer enhancement factor, i.e., the ratio of the real mass transfer coefficient to that predicted by penetration theory, can be raised up to 5- to 8-fold. Moreover, several scholars (Goldstein et al., 1990; Rahman et al., 2000; Rahman, 2001; Chen et al., 2014) conducted separate investigations focusing on mass transfer with natural convection and obtained empirical correlations for the mass transfer coefficient. In these correlations, the dimensionless *Sh* number is typically assumed to be correlated with the *Ra* number. However, recently, Guo et al. (2015) investigated the interfacial mass transfer of CO_2 absorption into an initially quiescent liquid layer with

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variations in layer height and found an obvious discrepancy between the mass transfer coefficient and the predicted value based on such correlations. Guo's work suggested that due to the complexity of the system, the model using the *Ra* number to predict the mass transfer rate is flawed. There is a need for a more precise mass transfer model, but so far, there is no consensus on the acceptable model applied to the Rayleigh convection despite intensive efforts devoted to this problem.

Abandoning the conventional *Sh*–*Ra* correlations means more sophisticated models have to be proposed to replace them, but the inadequate knowledge of mass transfer with interfacial convection hinders the proposal of new models. The other difficulty lies in the fact that very few studies have measured the velocity and concentration fields simultaneously, and thus, we lack verification of any guesses of how the velocity field affects mass transfer. Fortunately, progress is being made with the recent development of nonintrusive measurement techniques and powerful numerical simulation schemes. Chen et al. (2014) performed the particle image velocimetry (PIV) measurement for the velocity field in Rayleigh convection. Fu et al. (2011) employed a two-equation LBM in the computational solution of velocity and concentration fields of Rayleigh convection, and an experimental measurement of the velocity field was conducted via PIV. Fu et al. (2013) proposed the random disturbance model to mimic actual interfacial disturbance, which is necessary for the onset of Rayleigh convection. Furthermore, Chen et al. (2012) developed a hybrid Lattice-Boltzmann/finite-difference method (LBM–FDM) to simulate the concentration gradient-induced interfacial convection in gas–liquid systems. The simulation results, which were confirmed by the PIV experiments, reproduced the meso-scale flow behaviors and mass transfer characteristics. In addition, with the help of Schlieren observation and LBM–FDM, Chen et al. (2015) revealed the 3D features of interfacial convection in the CO_2–ethanol system. However, even now, it is still rather inconvenient to experimentally obtain the real-time velocity and concentration fields at the same time. Therefore, numerical simulation seems to be extremely important if it can provide reliable data. As stated above, the LBM-based numerical scheme is a reliable method. Because the method can provide believable data for the evolutionary velocity field versus the concentration field, a natural extension would be to build an elaborate model, which can reflect the inherent mechanism of mass transfer in the interfacial convection process.

In turbulent flow, there are several mass transfer models beyond the classical mass transfer models (Whitman, 1923; Higbie, 1935; Dankwerts, 1951), which emphasize the relation between mass transfer rate and velocity field. These models utilize the near-surface quantities as model parameters, e.g., the large eddy (Fortescue and Pearson, 1967) and the small eddy model (Banerjee et al., 1968; Lamont and Scott, 1970) utilize the energy dissipation as the model parameter; the surface divergence model (Banejee, 1990; Banejee et al., 2004) relates the surface divergence to the mass transfer; and many other models (McCready et al., 1986; Law and Khoo, 2002; Tamburrino and Gulliver, 2002; Wanninkhof, 1992; Zhao et al., 2003; Albert et al., 2004; Hu et al., 2014) use other near-surface quantities, such as the root-square-mean (rsm) fluctuating vertical velocity gradient, wind speed, wind-wave state or interfacial vorticity as the controlling hydrodynamic parameter. Despite the dearth of knowledge of the complex temporal-spatial velocity field in highly turbulent flow, the mass transfer rate predicted by these models is sufficient for industrial use.

The aforementioned turbulent mass transfer models are based mostly on the theory that the eddy in the turbulent flow represents the bulk of the mass transfer. In this point, the Rayleigh convection is analogous to the turbulent flow. In an example of the absorption of gas into a liquid layer in stationary contactor, which is commonly encountered in real situations, the cellular or chaotic convection occurs at the gas–liquid interface when the buoyancy of the liquid layer begins to overcome the viscous force, though the fluid layer is quiescent as a whole. Realizing that the essence of the turbulent flow is the eddy independent of its generation mechanism, the Rayleigh convection can be considered as a unique turbulent flow with zero mean velocity. It is from this viewpoint that it is appropriate to relate the hydrodynamic parameter to the mass transfer of Rayleigh convection, as is done by turbulent mass transfer models. In this study, some statistical hydrodynamic quantities are hypothetically applied to fit the LBM–FDM simulation results of the Rayleigh convection of CO_2 absorption into the solvents. To improve our understanding of interfacial mass transfer with convection, the authors attempt to extend this study by further fundamentally revealing the mass transfer mechanism, i.e., in what manner and to what extent the Rayleigh convection affects the interfacial mass transfer.

2. Numerical modeling

2.1. Numerical method

The hybrid LBM–FDM (Chen et al., 2012) is applied to simulate the Rayleigh convection. The velocity field is calculated using the LBM, which is based on the numerical solution of the Boltzmann equation and describes transport phenomena by tracking the propagation of the distribution functions of moving pseudo-particles.

The Lattice Boltzmann equation with BGK approximation represents the evolution equation of the particle distribution (Bhatnagar et al., 1954)

$$f_i(\mathbf{x}+\mathbf{c}_i\Delta t, t+\Delta t)-f_i^*(\mathbf{x},t) = -\frac{1}{\tau}[f_i^*(\mathbf{x},t)-f_i^{\mathrm{eq}}(\mathbf{x},t)] \tag{1}$$

where $\mathbf{x}$ is the position vector; $\mathbf{c}_i$ is the discrete velocity vector; Δt is the lattice time step; $\tau=\tau_c/\Delta t$, is the dimensionless relaxation time; and f_i and f_i^* represent, respectively the pre- and post-collision particle distribution functions with discrete velocity $\mathbf{c}_i$.

The present simulation is conducted with a D2Q9 model (Qian et al., 1992), as shown in Fig. 1, in which the discrete velocity $\mathbf{c}_i$ is defined as

$$\mathbf{c}_i = \begin{cases} (0,0) & i=0 \\ c\left(cos\left(\frac{(i-1)\pi}{2}\right), sin\left(\frac{(i-1)\pi}{2}\right)\right) & i=1-4 \\ \sqrt{2}c\left(cos\left(\frac{(i-5)\pi}{2}+\frac{\pi}{4}\right), sin\left(\frac{(i-5)\pi}{2}+\frac{\pi}{4}\right)\right) & i=5-8 \end{cases} \tag{2}$$

where $c=\Delta x/\Delta t$ is the lattice propagation speed and Δx and Δt are the lattice grid spacing and the time step, respectively.

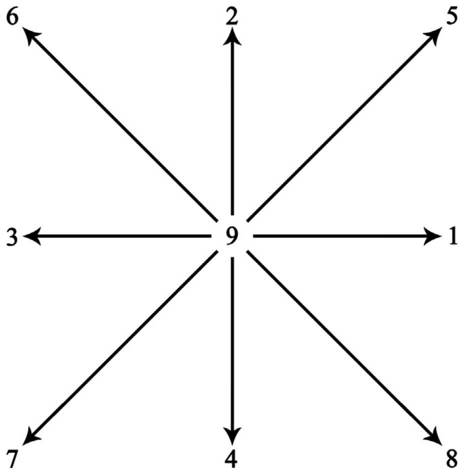

Fig. 1. Two-dimensional nine-velocity (D2Q9) model.