1 Introduction

Heat transfer between multiphase media and solid surfaces are encountered in applications as diverse as power generation, chemical processing, and biological systems. Examples are steam generators, vapor condensers, two-phase heat exchangers, distillation reboilers, fluidized bed reactors and combustors, and many others. In contrast to single-phase systems where basic transport mechanisms are mostly understood, the mechanisms for transport in multiphase systems still are mostly being developed. One reason for this is the complexity of interfacial contact at the surface, which is affected by intermolecular forces, varies with specific phases, influenced by dimensional scale, and is often of transient (dynamic) nature. One common cause of this complexity is the self-determining nature of phasic distribution found in multiphase media. Whether it’s solid/gas distribution in fluidized media, or vapor/liquid distribution in two-phase flows, the local concentration and morphology of individual phases usually are not known a priori. The hundreds of research papers that are published each year in leading journals and conference proceedings attest to the importance of this subject, as well as to its unfinished state of development.

To design transport systems, engineers use a variety of approaches ranging over the spectrum from the purely empirical to the deterministic. From the viewpoint of applications, any approach (or combination of approaches) is acceptable if it promotes sound engineering design. Some well-known approaches can be located along this spectrum, as illustrated in Fig. 1. The placement of any single approach is a matter of judgment and subject to personal opinion. For example, one could argue that Fourier’s law of conduction is a basic principle and should be placed toward the deterministic end of the spectrum. However, we note that when Josef Fourier published his treatise in 1822, he described the proportionality between conductive heat flux and temperature gradient as just an empirical relationship (see Lienhard [1]). With better understanding of single-phase transport phenomena, more deterministic approaches are available for such systems, e.g., the Graetz solution for laminar convection. In contrast, design of multiphase transport systems currently rely heavily on heuristic experience, e.g., correlations for boiling curves. Fortunately, if one can identify the domain of governing parameters for surface contacts in a specific multiphase system, the difficulty of engineering design is much lessened. Whether it’s parameters in spatial, time, energy, or other domains, once recognized we can utilize a combination of heuristic knowledge and phenomenological models for engineering design and/or to improve the transport process. This paper seeks to illustrate this point with examples from two diverse systems—heat transfer in fluidized beds and droppwise condensation.

2 Heat Transfer in Fluidized Beds, Significance of Parameters in Time Domain

2.1 Background. Fluidized bed is a unit operation in which gas flows upward through a bed of solid particles, suspending the particles against gravitational body force. The particles may remain suspended in the bed for a long residence time (dense-bubbling fluidized bed) or be transported through the bed with a short residence time (fast fluidized bed). In either case, the solid-gas contact is utilized to promote either physical processes such as heating/cooling, or chemical processes such as combustion or catalytic cracking (Kunii and Levenspiel [2]). In spite of its commercial success, the technology of fluidization still relies heavily on empirical knowledge, e.g., correlations for boiling curves. Fortunately, if one can identify the domain of governing parameters for heat transfer to/from surfaces submerged in bubbling fluidized beds, parameters in time domain are most important. In the case of condensation, it is shown that substantial enhancement of heat transfer coefficient can be obtained by controlling parameters in the domain of surface free energies. [DOI: 10.1115/1.1566050]
on heuristic knowledge with little in way of unifying theories. Merrow [3] estimates that manufacturing processes that involve solid particles often reach no more than 60% of their design capacity, far inferior to processes that deal with single-phase gases or liquids.

Many fluidized bed applications require thermal control by extraction or addition of thermal energy (e.g., heat removal in fluidized combustors). For this purpose, tubes carrying cooling/heating fluids are often immersed in the fluidized bed, hence requiring knowledge of the heat transfer coefficient \( h \) at the immersed (tube) surfaces for engineering design. Most applications rely on experimental measurements, which have been reported by various authors [4–10]. Typical results are illustrated by the sample data of Ozkaynak and Chen [4] for spherical glass particles fluidized in ambient air, replotted in Fig. 2. Significant characteristics are:

- Heat transfer coefficient \( h \) increases steeply as gas velocity exceeds minimum fluidization velocity \( (U_{mf}) \).
- The heat transfer coefficient attains maximum magnitude at some specific velocity that varies with particle size.
- Beyond the maximum point, \( h \) declines slightly with further increase of gas velocity.
- Absolute magnitude of \( h \) is several fold greater than obtained by single-phase gas convection at similar velocities.
- The heat transfer coefficient decreases with increasing particle size.

Heat transfer tubes located vertically in the fluidized bed, as the case for data of Fig. 2, have axial symmetry due to alignment with gravitational body force. Tubes located horizontally do not have such axial symmetry and one finds significant variations of the local coefficient around the tube circumference. Chandran et al. [5] reported variations up to 500% in \( h \) at different positions on the tube surface, for a given operating condition.

### 2.2 Models

To date, there is no universally accepted theory for the mechanisms of heat transfer in fluidized beds. It is generally recognized that gaseous convection, conduction through contacting particles, and thermal radiation can all contribute to heat transfer between the fluidized medium and immersed surfaces. For most applications, the combined “convection” due to gas and particles is the major contributor and has been the objective of predictive models.

A common approach assumes similarity to gaseous convection and assigns thermal resistance to a boundary layer at the heat transfer surface [6,8,9–11]. The enhancement found at gas velocities greater than \( U_{mf} \) is attributed to “scouring by solid particles, decreasing the effective film thickness.” Models following this approach attempt to correlate a Nusselt number with the fluid Prandtl number, a modified Reynolds number and the Archimedes number, using either the particle diameter (\( d_p \)) or the tube diameter (\( d_t \)) as the characteristic length dimension. This approach has led to dozens of empirical correlations, an example being the correlation of Borodulya et al. [11].

\[
\text{Nu} = 0.74 (\text{Ar})^{0.1} \left( \frac{\rho_s}{\rho_g} \right)^{0.14} \left( \frac{c_p s}{c_p g} \right)^{0.24} \left( 1 - \varepsilon \right)^{0.67} \\
+ 0.46 (\text{Re}_p \text{Pr}_g) \left( 1 - \varepsilon \right)^{0.67} \frac{1}{\varepsilon} 
\]

where,

\[
\text{Nu} = \frac{h d_p}{k_g} \\
\text{Re}_p = \frac{d_p \rho_g U}{\mu_g} \\
\text{Ar} = \frac{g d_p^4 (\rho_s - \rho_g)}{\rho_g \nu^2} \\
\varepsilon = \text{void fraction, volume fraction gas.}
\]

Figure 3, modified from Chen [12], compares several different correlations against each other and against a set of experimental data, for ambient-pressure fluidization of 240-micrometer glass beads. It is seen that there is very little agreement between the various correlations and with data, with deviations of order 100%. A fairly recent model suggested by Molerus and Schweizer [13] considers gas convection through the matrix of particles in vicinity of the heat transfer surface. This model resulted in a dimensionless correlation for the Nusselt number in terms of the Archimedes number and the fluid Prandtl number, at velocities above \( U_{mf} \). This correlation was limited to large particles (i.e., Geldart group D particles) and would significantly under-predict the data of Fig. 3. While all such empirical, convective correlations are easy to use, their generality is questionable.

A variation of the convective model is that of Martin [14–16] who proposed an analogy between particle motion in fluidized beds and random motion of gaseous molecules. Utilizing kinetic theory of gases, Martin developed a model with just one empirical parameter to predict heat transfer coefficients in fluidized beds. Good results were reported when the model was compared with experimental data from several sources (Martin [16]). Despite this success, the kinetic theory analogy has been challenged by investigators who note that the nature of alternating contacts between particle emulsion and gas bubbles in fluidized beds is qualitatively different than that of contact by particles in random motion.
For “large” particles, typically with diameters greater than 1 mm, whose thermal response time is long, a contact resistance approach has been suggested. Such models assume that the average temperature of particles does not change while in contact with the heat transfer surface, and thus utilize pseudo-steady-state conduction analysis. Adams and Welty [17] analyzed gas convection enhanced conduction in the interstitial channels between the surface and particles, resulting in numerical solutions for distribution of Nusselt numbers around horizontal tubes. In a similar vein, Decker and Glicksman [18] utilized empirical correlations for convective heat transfer of packed beds to estimate the convective/conductive transfer of particles on surfaces submerged in fluidized beds. Clearly, such approaches are unlikely to be valid for fluidization of small or medium size particles as encountered in many chemical and combustion applications.

2.3 Mechanisms and Time Domain Effect. Mechanistically speaking, it is questionable if steady-state convection is an accurate analogy for heat transfer in fluidized beds. Visual observations in actively bubbling beds indicate that the particle emulsion actually remains fairly static, until disturbed by discrete gas bubbles rising through the bed. Phenomenologically, the best model for fluidized bed heat transfer may well be the “packet model” suggested by Mickley and Fairbanks [19] nearly half a century ago in 1955. They considered the heat transfer surface to be alternately contacted by gas bubbles and an emulsion of closely packed particles (packets). This leads to a surface renewal process whereby heat transfer occurs primarily by transient conduction between the emulsion packets and the surface during periods when the particle packets reside at the heat transfer surface. One then would need to know the distribution of packet residence times and the fraction of total time with packet contact—hence attention is focused on parameters in the time domain.

Three decades after Mickley and Fairbank’s paper, this basic concept was experimentally confirmed by researchers who were able to measure transient variations of particle concentration at heat transfer surfaces. Surface capacitance sensors with flush mounted electrodes of the type shown in Fig. 4, redrawn from Ozkaynak and Chen [20], utilized the difference of dielectric constants between gas and solids to obtain real-time measurements of fluctuating particle concentration at surfaces immersed in fluidized beds. With appropriate electronic circuits operating in range of several hundred kilohertz, such sensors had response times several orders of magnitude faster than the characteristic time scale of particle dynamics.

Figure 5 shows a sample trace obtained by Chandra and Chen [21], indicating the transient variation of particle concentration at sides of a horizontal tube immersed in a fluidized bed of glass beads (mean diameter of 245 micrometers), operating at superficial air velocity of 0.63 m/s (12 times minimum fluidization velocity). It is seen that the particle concentration is highly dynamic, varying dramatically over time. It is also seen that the instantaneous concentration alternated between almost pure gas (bubble phase) and high concentration approaching that of packed beds (emulsion packet phase). This is the behavior hypothesized by Mickley and Fairbanks. Such evidence of highly transient contacts lends support to the surface renewal model, where the time average heat transfer coefficient \( \langle h \rangle \) has proportional contributions from the bubble phase coefficient \( \langle h_b \rangle \) and packet phase coefficient \( \langle h_p \rangle \),

\[
h = (1 - f_p)h_b + (f_p)h_p
\]

where \( f_p \) is the fraction of time when surface is in contact with the dense packet phase. Treating the particle packet as a pseudo-homogeneous medium of solid volume concentration \( (1 - \epsilon)_p \), Mickley and Fairbanks’ transient conduction analysis yielded the following equation for average packet coefficient,

\[
h_p = \left[ \frac{k_p \rho \epsilon \rho_s (1 - \epsilon)_p \frac{1}{\tau_p}}{\pi} \right]^{1/2}
\]

where \( \tau_p \) is the root-mean residence time of packets at the heat transfer surface,

\[
\tau_p = \frac{\sum_{i=1}^{n} (\tau_p)_i^2}{\sum_{i=1}^{n} (\tau_p)_i}
\]

for stochastic number of \( n \) packets.

If one accepts the fact that \( h_b \) is small in comparison to \( h_p \), then the Mickley-Fairbank model reduces to the following equation for effective heat transfer coefficient in bubbling fluidized beds,

\[
h \equiv f_p h_p = 2 f_p \left[ \frac{k_p \rho \epsilon \rho_s (1 - \epsilon)_p \frac{1}{\tau_p}}{\pi} \right]^{1/2}
\]

All parameters in Eq. (5) can be evaluated from properties of the solid particles and gas, with the exception of the two time-domain parameters \( f_p \) and \( \tau_p \). Therein lies the difficulty. These two im-

![Surface Capacitance Probe](Redrawn from Ozkaynak & Chen, 1978)
Fig. 5 Capacitance signal of particle concentrations at heat transfer surface in bubbling fluidized bed

Important parameters in the time domain depend on the multiphase fluid dynamics of the fluidized bed and to a large extent are not known a priori.

Some limited information on these time parameters were obtained using the capacitance-sensors and have been reported in the open literature. For the case of vertical tubes in bubbling beds, Ozkanak and Chen [4] found that the probability distribution of residence times for particle packets is log normal. The root-mean residence times vary with particle density, particle size, gas properties, gas velocity and bed geometry. Figure 6 plots some of their experimental results, showing that the mean residence time ($\bar{t}_p$) increases with particle diameter ($d_p$). These data also indicate exponential decrease of the mean residence time with increasing excess gas velocity above minimum fluidization velocity, $U-U_{mf}$. The latter characteristic is consistent with observations that excess gas velocity increases bubble frequency, so that packets residing on the heat transfer surface are more frequently displaced. In a similar vein, Ozkaynak and Chen [4] reported measurements of the time fraction when the heat transfer surface is covered by particle packets ($f_p$), as replotted in Fig. 7. The time fraction is seen also to increase with particle size, and decrease with excess gas velocity.

The situation for heat transfer tubes placed horizontally in fluidized beds is even more complex and unknown. Measurements of parameters in the time domain reported by Chandran and Chen [21] indicate that the absence of axial symmetry causes large variations in both time-fraction ($f_p$) and residence-time ($\tau_p$) around the tube circumference, with resultant variations in the heat transfer coefficient ($h$). These authors attempted correlations for $f_p$ and $\tau_p$, but recognized that much more data are required before any general correlations could be realized.

The data of Fig. 6 implies an added complication in the time domain. With residence times of order $<1$s, the Fourier modulus for transient conduction in the particle packets would be of order,

$$F_D = \frac{k_p \tau_p}{\rho_p c_p (1 - e_p) d_p} \approx O(10)$$

(6)

This magnitude of the Fourier modulus implies that the conduction waves in the emulsion packets may penetrate distances of only a few particle diameters during the residence period, $\tau_p$. Since packing density of particles is reduced in the first layer of particles at a solid wall, one should account for the corresponding reduction of effective thermal conductivity in this near-surface region. It is therefore desirable to modify the Mickley-Fairbanks’ packet model, originally proposed for emulsion packets with uniform voidage and properties. Chandran and Chen [22] obtained numerical solutions of the transient conduction problem, resulting in a correction factor ($C_x$) to account for this variation of thermal conductivity in the first layer of particles at a surface. An easier approach is to use effective packet properties, taken at one-half the penetration depth of the temperature wave for the given operating condition.

From solution of the transient conduction equation, we find the penetration depth ($\xi$), defined as the distance into the packet emulsion where 90% of the temperature change is obtained in residence time $\tau_p$, to be given by

$$\text{erf} \left( \frac{\xi}{2 \sqrt{\alpha_p \tau_p}} \right) = 0.9$$

$$\xi \equiv 2.32 \sqrt{\alpha_p \tau_p}$$

(7)

where

$$\alpha_p = \frac{k_p}{\rho_p c_p (1 - e_p)}.$$  

(8)

At positions within one particle diameter of the heat transfer surface, we can use an approximation of the local void fraction by fit to the results of Kubie and Broughton [23],

$$e_x = 1 - 2.04(1 - e_p) \left( \frac{x}{d_p} \right) \left( 1 - 0.51 \frac{x}{d_p} \right).$$  

(9)

At positions greater than one $d_p$ from the surface, the local void fraction and packet properties are equal to the values at bulk emulsion voidage, $e_p$. It is suggested that the packet model of Mickley and Fairbanks be modified for cases where $\xi/2 < d_p$ by taking effective thermal conductivity of the emulsion packet at
2.4 Further Developments. Further development of this approach depends on the acquisition of knowledge about the two time-domain parameters, \( \tau_p \) and \( f_p \). Lacking such, it is still impossible to calculate heat transfer coefficients a priori, for engineering design. The goal is to obtain sufficient knowledge for prediction of \( \tau_p \) and \( f_p \) for process conditions (e.g., solid and gas properties, system geometry, gas velocity) in any application. This author suggests that this goal can be attained by a combination of two tasks.

First, the technical community can collect an extended database of experimental measurements of \( \tau_p \) and \( f_p \), over wide range of operating conditions. Empirical correlations can then be developed for these two time-domain parameters, and utilized in the modified packet model for calculation of heat transfer coefficients. The capacitance sensing technique, as referenced above, is one means for achieving such measurements. Other techniques, e.g., optical probes, may also prove to be useful. The range of experimental conditions needs to cover conditions of anticipated applications, including variations in gas pressure and temperature, as well as different type/size of particles and different bed geometries.

A second, complimentary task is to develop deterministic models for the dynamics of particle movement in fluidized beds. Such models must correctly represent particle-fluid, particle-particle, and particle-wall interactions. In recent years, promising progress has been made with two types of multi-phase models. Firstly, continuum models using local averaging at the scale of the computational cell have treated the gas and solid phases as interpenetrating continuum media. These constitutive relations, mostly of empirical nature, are required to obtain closure of the problem. Van Wachem et al. [28] concluded that the selection of specific constitutive relationships could alter the model predictions significantly. Quoting these authors, “—we have shown how the hybrid drag model proposed by Gidaspow [26] produces a discontinuity in the drag coefficient, how an order-of-magnitude difference in the normal stress is predicted by the various frictional stress models—.” Another difficulty for the present objective is the mechanical averaging at scale of computational cell is usually too coarse to follow dynamic variations of particle emulsion at heat transfer surfaces. Excellent reviews of the potentials and limitations of such CFD models are given by van Wachem, J. C. Schouten et al. [28] and by Arastoopour [29].

An alternate to the continuum model is the discrete particle model (DPM) using Lagrangian formulation. Introduced by Cundall and Strack [30] for granular flow, DPM tracks the motion of particles by direct application of Newton’s second law of motion to the collision process of individual particles. This approach provides deterministic representation of particle-particle and particle-wall interactions. In the recent decade, researchers have extended other increases of gas velocity. Comparing Fig. 8 and 3, it is seen that this modified packet model is substantially better than the empirical convective models in its ability to calculate effective heat transfer coefficients for fluidized beds. Of course, additional comparisons with more extended data would be very desirable.

Based on this limited assessment, we suggest the following conclusion: Heat transfer to surfaces submerged in bubbling fluidized beds is governed by parameters in the time domain, namely the mean residence time (\( \tau_p \)) and the time-fraction of residence (\( f_p \)) of emulsion packets at the surface. With information on these two parameters, the modified packet model can provide predictions of the heat transfer coefficient, \( h \).

Fig. 8 Comparison of modified packet model, using time domain parameters, with experimental data for heat transfer in bubbling fluidized beds

The modified “packet model” is then given by Eqs. (5, 10, 11, or 12).

At present time, there are insufficient measurements of the key time parameters \( f_p \) and \( \tau_p \) to fully test this model. However, it is appropriate to ask the question: for cases where the time-domain parameters are known, can the packet theory accurately predict heat transfer coefficients? Equation (5) indicates that decreasing \( f_p \) and \( \tau_p \) has opposite effects on magnitude of \( h \). Would the trends indicated in Figs. 6 and 7, when applied to Eqs. (5, 10, 11, or 12), give correct magnitude and trend for the effective heat transfer coefficient, \( h \)? To test this, we can use the data for \( \tau_p \) and \( f_p \) shown in Figs. 6 and 7 in equations (5, 10, 11, or 12) and compare the calculated values of \( h \) to the experimentally measured heat transfer coefficients of Fig. 2. This was done, based on the mean curves for \( \tau_p \) and \( f_p \) shown in Figs. 6 and 7, respectively. These values of the time parameters were then utilized in the modified packet model, equations (5, 10, 11, or 12), to calculate predicted values for the heat transfer coefficient, \( h \). Results are compared to experimental values of \( h \) in Fig. 8, over a range of gas velocities and for two different sizes of particles. While the agreement is not perfect, the comparison is quite satisfactory. The modified packet model gives good representation of the magnitudes of \( h \), as well as the trends for parametric variations with gas velocity and particle size. For a number of sizes, the modified model calculated increasing \( h \) as gas velocity exceeded \( U_{mf} \), reaching a maximum at some intermediate velocity, and then decreasing slowly with further increases of gas velocity.
the DPM approach to account for fluid-particle interactions, concentrating initially on the drag force exerted by the fluid upon particles (see for example Tsuji et al. [31], Drake and Walton [32], Langston et al. [33]). More recently, several researchers further extended DPM models to account for effects of mutual momentum transfer between the fluid and particle phases, thus making this approach useful for fluidized beds where such interaction is important. The simultaneous tracking of particle collisions and gas motion calls for the direct integration of the Lagrangian discrete particle model with the Eulerian CFD continuum model. With various simplifying approximations, Tsuji et al. [34] and Hoomans et al. [35] have successfully applied this approach to model bubbling fluidized beds, with some limitations. Xu and Yu [36] and Xu et al. [37] were able to relax some of these limitations with more rigorous combination of CFD with DPM, using a collision dynamic model that better represents stiff particles. These researchers also introduced Newton’s third law of motion to obtain a rigorous coupling between the particle scale of DPM and the larger cell-scale of CFD. Van Wachem, J. van der Schaaf et al. [38] compared Lagrangian-Eulerian simulations with experiments and concluded that two-dimensional simulations are in fair agreement with experiments but that three-dimensional simulation is required to capture more precisely the behavior of fluidized beds. While a detailed review of such Lagrangian-Eulerian models is beyond the scope of the present paper, a brief synopsis is warranted, in view of the promise of this approach for advancing the state of art toward prediction of heat transfer in fluidized beds. The essential discrete particle model (DPM) is the conservation of linear and rotational momentum of the particles as they undergo particle-particle, particle-wall and particle-gas interactions. Following Xu and Yu, [36], this can be expressed by Newton’s 2nd law of motion for a particle,

\[ m \frac{dv_i}{dt} = m_i \mathbf{g} + f_{ci} + \sum_{j=1}^{k} (f_{cij} + f_{dij}) \] (13)

\[ I_{i} \frac{d\omega_{i}}{dt} = \sum_{j=1}^{k} \mathbf{T}_{ij} \] (14)

where \( m_i \), \( v_i \), \( I_i \), \( \omega_i \) are the mass, linear velocity, moment of inertia, and rotational velocity of particle \( i \), respectively. Forces acting upon particle \( i \) are the gas drag force \( f_{ci} \), the contact force between particles \( i \) and \( j \) \( f_{cij} \), and the contact damping force between particles \( i \) and \( j \) \( f_{dij} \). \( T_{ij} \) is the torque generated by interparticle contact, as measured to the mass center of particle \( i \). On the fluid side, using local mean variables over a computational cell, computational fluid dynamics (CFD) are based on the continuity and Navier-Stokes equations,

\[ \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \] (15)

\[ \frac{\partial(\rho \mathbf{v})}{\partial t} + \nabla \cdot (\rho \mathbf{v} \mathbf{v}) = -\nabla p - \mathbf{F} + \nabla \tau + \rho \mathbf{g} \] (16)

where \( \rho \), \( \mathbf{v} \), \( p \), \( \mathbf{F} \), \( \mathbf{g} \), \( \tau \) are the gas density, velocity, pressure, respectively. \( \mathbf{F} \) is the volumetric interaction force between gas and particles, and \( \tau \) is the viscous stress tensor. To obtain closure of this problem, one needs specific descriptions (constitutive relations) for the various terms in Eqs. (13–16). Much of the science and art for these combined Lagrangian-Eulerian models lies in the formulation of these constitutive relations, and the reader is referred to the works of Xu and Yu [36], Hoomans et al. [35], and Xu et al. [39].

Numerical simulation of bubbling fluidized beds requires significant computing power, and this is on the horizon as larger parallel computing systems become available. At the time of this writing, researchers have successfully achieved two-dimensional simulations with \( O(10^4) \) number of particles. While this level is not quite sufficient for our purpose of predicting heat transfer coefficients on submerged surfaces, the qualitative results show good promise. Figure 9 presents simulation results obtained by Xu and Yu [36] for a two-dimensional bed (15 cm width) of 4.0 mm diameter particles, fluidized at superficial gas velocity of 2.8 m/s by a single gas jet. It is seen that characteristic bubbling behavior is obtained. Figure 10 shows dynamic variations of void fraction, obtained by simulation for a two-dimensional bed of particles fluidized by atmospheric air. The gradations of color and shade indicate instantaneous voidages in the bed. One can expect that if a heat transfer tube were submerged in this bed, the simulation would predict the dynamics of alternating contact with gas bubbles and packets of particle emulsion. While this figure presents only 0.09 seconds of the transient dynamics, it is obvious that simulate particle motion would have required even longer time duration would give stochastic information on the time-domain variables of interest, \( \tau_p \) and \( f_p \), for any Eulerian control volume at the heat transfer surface. While such simulation results would need to be confirmed by comparison to experimental data, one hopes that success can be achieved with ever improving models.

In conclusion, we can anticipate in the future that the accumulation of experimental measurements and numerical simulation results for the time-domain parameters, mean residence time \( \tau_p \) and time fraction \( f_p \), will enable the engineering community to utilize the modified packet model to obtain a priori predictions of heat transfer coefficients in bubbling fluidized beds.

3 Dropwise Condensation, Significance of Parameters in Surface Energy Domain

3.1 Background. It is known that vapor in contact with a cold surface of temperature below saturation dew point can condense on that surface as a liquid film, as liquid drops, or as a mix of the two patterns. Filmwise condensation occurs when the condensed liquid wets the solid surface, entire uncolored surfaces, most likely on ones with high free energies. Dropwise condensation occurs when the solid surface has low free energy and is poorly wetted by the condensate liquid. Observations of dropwise condensation indicate a highly transient, cyclic process—the condensate nucleating as small droplets on the cold surface, which then grow and coalesce into larger drops. When the large drops reach a size sufficient to be removed from the surface by external forces (e.g., gravity or wind shear), they tend to sweep over the surface, absorbing and wiping small droplets in their path. New droplets then form and grow on the wiped surface, repeating the cyclic process. Figure 11 shows a normal-view photograph of dropwise condensation, from Lienhard [1]. It is seen that at a given moment, drops of various sizes exist on the solid surface. In Fig. 11, one can particularly note the region above the large central drop, showing a path that was wiped by passage of that large drop in which smaller drops are nucleating and starting to grow. On dimensional scale of drops, the heat transfer process is highly transient over time and variable over space. However, on the system scale, a large number of drops and droplets would exist on the solid surface at any one time, each in its own history of nucleation, growth and removal. Over a sufficiently large surface, one can thus anticipate an average heat transfer behavior that is essentially at steady state for a given set of process conditions.

A condensation heat transfer coefficient is commonly defined as the ratio of surface heat flux to the degree of subcooling temperature on the surface,

\[ h = \frac{q}{\Delta T_i} \] (17)

where \( \Delta T_i = T_i - T_w \). In filmwise condensation, the heat flux is controlled by the thermal resistance of the liquid film and therefore the mechanism of film removal directly affects the heat transfer coefficient. In case of film condensation on a vertical wall, where gravitational body force causes film removal, the classic
Fig. 9  Numerical simulation of fluidized bed by combined Eulerian-Lagrangian model [36]

(Air fluidized bed of particles with $d_p=550\mu m$, $\rho_p=2,500$ kg/m$^3$)

Fig. 10  Void fractions obtained from combined Eulerian/Lagrangian simulation model for a bubbling fluidized bed [39]
Nusselt analysis (1916) [40] gives good predictions for laminar films. In the case of external condensation on a horizontal tube, the average Nusselt number is given by,

\[ Nu_l = \frac{h_c LD}{k_f} = 0.729 \left( \frac{\rho_v (\rho_v - \rho_e) h_w}{\mu_k k_f} \right) \left( \frac{g D^3}{\Delta T_s} \right)^{1/4} \]  

(18)

The reader is referred to various heat transfer textbooks for extensions of the Nusselt analysis to turbulent films and other wall geometries, e.g. Lienhard, [1].

The dropwise condensing coefficient can be significantly greater than corresponding filmwise coefficient, as illustrated in Fig. 12 by data of Marto et al. [41] for horizontal tubes. In their experiments, Marto et al. achieved dropwise condensation by coating the metal tube surface with a thin layer of fluoroacrylic. It is seen from Fig. 12 that dropwise condensation attained heat transfer coefficients over three times greater than those in filmwise condensation. It is also notable that these results indicate \( h_c \) for dropwise condensation to be essentially constant, independent of heat flux \( q \), and therefore of the subcooling \( \Delta T_s \).

3.2 Models. The mechanism for heat transfer in dropwise condensation is still in debate. One premise is that there actually exists a liquid microfilm, of order <1 \( \mu \)m thickness, on the solid surface. As the thickness increases due to condensation, a critical thickness is reached at which surface tension of the liquid causes rupture of this microfilm, and formation/coalescence of drops. A new microfilm is presumed to quickly form over the uncovered wall surface. Condensation then continues on the growing drops and on the microfilm between drops. This model, here termed the “micro-film model,” was initially proposed by Jakob in 1936 [42] and followed-up by several researchers in subsequent decades, e.g., Welch and Westwater [43], Sugawara and Katusuta [44].

A different model starts with the premise that when the subcooled surface is poorly wetted by the liquid phase, micro-drops of condensate nucleate heterogeneously at selected sites on the solid surface. This concept is analogous to the premise for heterogeneous nucleation of vapor bubbles on superheated surfaces in boiling, and has gained support in recent years. The experimental evidence of Umur and Griffith [45] confirmed that the surface area between condensate drops remains dry with no indication of a microfilm. Thus, this model presumes a cyclic process of droplet nucleation at active sites, growth by mass addition due to condensation, coalescence due to surface tension effects, and finally removal by body force or shear drag. Since its early proposal by Eucken [46], this “nucleation model” has been further developed by a number of authors in recent years, e.g. Graham and Griffith [47], Rose and Glicksman [48], Tanaka [49], Rose [50], Wu et al. [51].

Following the concept of the nucleation model, heat transfer during dropwise condensation would occur by conduction through the drops and by vapor convection on the bare solid surface. The first path generally dominates and has been the focus of attention for most models. As described by Graham and Griffith [47], vapor condensing on a drop surface releases latent heat, which is conducted through the liquid drop to the solid surface, to be then dispersed through the substrate. For condensation of pure vapor on an isothermal surface, and neglecting the minor subcooling energy of liquid in the drop, the overall temperature driving force \( \Delta T_s \) is comprised of the temperature drops associated with three resistances,

\[ \Delta T_s = \Delta T_t + \Delta T_{ic} + \Delta T_i \]  

(19)

where \( \Delta T_t \) is the temperature drop due to conductive resistance in the liquid drop, \( \Delta T_{ic} \) is the depression of saturation temperature associated with curvature of the vapor/liquid interface, and \( \Delta T_i \) is the temperature drop associated with mass transfer resistance at the interface. From thermodynamic and heat flow principles, the following expressions have been derived for the three temperature differences for a hemispherical drop of diameter \( D \) (see Graham and Griffith, [47], Carey, [52]):

\[ \Delta T_t = \frac{Q_d}{2 \pi DK_i} \]  

(20)

\[ \Delta T_{ic} = \frac{D_m}{D_k} \Delta T_s \]  

(21)

\[ \Delta T_i = 2 Q_d / (\pi D^2 h_i) \]  

(22)

where \( Q_d \) is the rate of heat transfer to the hemispherical drop, \( D_m \) is the diameter of the minimum stable drop, given by

\[ D_m = \frac{4 \sigma T_s}{\rho_v h_i \Delta T_s} \]  

(23)

In Eq. (22) \( h_i \) is the heat transfer coefficient at the liquid/vapor interface, derived to be

\[ h_i = \frac{\rho_v h_t}{T_t} \left[ \frac{2 \alpha}{2 - \alpha} \right] \left( \frac{M}{2 \pi RT_v} \right)^{1/2} \]  

(24)

where \( \alpha, M, \) and \( R \) are the accommodation coefficient at interface, molecular weight, and universal gas constant, respectively. Combining Eqs. (19–22), we obtain the following equation for rate of heat transfer to the drop of diameter \( D \),

\[ Q_d = \pi D^2 \left[ \frac{1 - \frac{D_m}{D} \frac{2}{2k_i + h_i}}{\frac{2k_i}{D}} \right] \Delta T_s \]  

(25)
The wall heat flux under the footprint of a drop with diameter \( D \) is then,

\[
q_d = \frac{4Q_d}{\pi D^2} = 4\left[\frac{1 - \frac{D_m}{D}}{\frac{2}{2k_l} + \frac{2}{h_l}}\right] \Delta T_s. \tag{26}
\]

From Eqs. (26) and (23), one can determine the relative effectiveness of various size drops for condensation heat transfer. Figure 13 shows the sensitivity of \( q_d \) to drop size \( D \), for water vapor condensing at atmospheric pressure. It is seen that the smaller drops are much more effective, with a decrease of two orders of magnitude in \( q_d \), as \( D \) increases from 0.01 mm to 1 mm. The reason is attributable to the shorter path length for heat conduction in the condensate liquid in the case of smaller drops. Further implications of this behavior will be examined below.

The heat flux due to \( n_D \) drops of diameter between \( D \) and \( D + dD \) per unit wall surface area is,

\[
dq = n_D q_d dD \tag{27}
\]

and the total heat flux on the wall surface would be the integral over the entire range of drop sizes,

\[
q = \int_{D_m}^{D_s} n_D q_d dD \tag{28}
\]

Neglecting the heat transfer to dry areas on the surface (usually small), the dropwise condensation heat transfer coefficient is thus obtained as,

\[
h_c = \pi \int_{D_m}^{D_s} n_D D^2 \left[1 - \frac{D_m}{D} \right] \frac{D}{2k_l + \frac{2}{h_l}} dD \tag{29}
\]

This model is formulated for a wall of isothermal temperature \( T_s \), a reasonable approximation for solids of high thermal conductivity and reasonable thickness. For thin walls or walls with low thermal conductivity, there may be significant conduction resistance associated with lateral conduction resistance in the wall material, (see Mikic [53]).

To apply this model of dropwise condensation, Eq. (29), one needs information on \( n_D \), the distribution of drop density by drop size. Graham and Griffith [47] used a microscope camera to measure the population density by drop size, for condensation of steam on a vertical copper surface. Some of their data, for water at atmospheric pressure, are recalculated in terms of the density \( n_D \) and plotted in Fig. 14. Unfortunately, physical constants of the equipment limited measurements to drops of \( D > 10 \mu m \). For smaller drops, with diameters less than 10 \( \mu m \), the investigators “guessed” a distribution to match measured heat fluxes, as indicated on Fig. 14. These authors further determined that the small drops are extremely important, with over 50% of the heat transfer being associated with drops of \( D \) less than 10 microns, beyond the range of experimentally measured drop densities.

Other authors have attempted to develop models for the drop density. LeFevre and Rose [54] suggested an empirical function to represent the distribution in terms of the fraction of wall surface area covered by drops of diameter between \( D \) and \( D_s \),

\[
f_D = 1 - \left(\frac{D_s}{D_m}\right)^b \tag{30}
\]

where \( D_s \) is the diameter of largest drop on the surface, and \( b \) is an empirical constant assigned value of 0.33 by these authors. This function gives the following expression for drop density distribution,

\[
n_D = \frac{4b}{\pi D_s^4} D \left(\frac{D_m}{D_s}\right)^{b-1}. \tag{31}
\]

Rose and Glicksman [48] proposed a model for the cyclic growth history of drops, thence obtaining estimates of \( n_D \) and concluding that their results can be approximated by using a value of 0.382 for \( b \) in Eq. (30) and (31). Their correlation is shown as the solid line on Fig. 14, indicating reasonable agreement with the data of Graham and Griffith for water condensing on vertical surface. Most recently, Wu et al. [51] used a random fractal model to obtain drop size distribution, matching their results by numerical simulation to heat transfer data reported in literature.

Mechanistically, it is self-evident that the steady-state distribution of drop sizes results from a balance of the transient dynamics for drop nucleation, growth, coalescence, and removal. Many, many parameters would affect this balance, including properties of the fluid and surface, as well as geometric and operational conditions. For example, any mechanism that increases retention of large drops on the surface, e.g., surface tension effects, would increase the fraction of larger drops. Conversely, mechanisms that aid removal of drops, e.g., external body force or shear force, would increase the frequency of drop removal and increase the fraction of smaller drops on the surface at any moment. The interaction of these parameters is highly complex and would be dependent of system variations. As Graham and Griffith concluded in 1973 [47], “It is a disappointment in that a simple, universal dropwise condensation heat transfer correlation appears to be out of reach. Separate drop distribution curves will be needed for high and low pressure and for each fluid-material combination.” This view is especially valid for any dropwise condensation under “non-typical” conditions, where all empirical models of \( n_D \) for “typical” conditions would be inapplicable.

One class of nontypical conditions is where drop formation is deliberately promoted by specific modification of material proper-
ties. Indeed, motivated by the promise for high heat transfer coefficients, many researchers have attempted to promote dropwise condensation. Almost all such efforts utilize the sensitivity of drop formation on “wetting” behavior of the fluid-solid interface, i.e., on surface tensions and surface energies. This leads us to consider the significance of parameters in the domain of surface energies.

3.3 Effects in Domain of Surface Energies. The fundamental basis for surface energies arises from intermolecular forces. In review of basic concepts, recall that intermolecular forces are considered to consist of a short range repulsive force and longer range electrostatic, inductive and dispersive attractive forces, commonly referred to as the van der Waal forces. The well known Lennard-Jones potential (Hirschfelder [55]) represents the summation of these forces by the equation,

\[ \phi_{ij} = 4\epsilon \left( \frac{r_{mi}}{r} \right)^{12} - \left( \frac{r_{mi}}{r} \right)^{6} \]  

(32)

where \( r \) is the intermolecular spacing and the parameters \( r_{mi} \), \( \epsilon \) vary with molecular specie. In the liquid near a vapor interface, the molecules are space slightly further apart than in the bulk liquid. This has little effect on the longer-range attractive forces, but significantly reduces the short-range repulsive force. With the discontinuity at the interface, there results a net force on liquid molecules in direction normal to the interface, that tends to pull toward the bulk liquid volume. In directions parallel to the interface, symmetry exists about each molecule so that there is no net force vector parallel to the interface. Instead, there results a net tension force on the molecules, equal in all directions parallel to the interface—hence, “surface tension” of the liquid in contact with its vapor \( (\sigma_{lv}) \). Thermodynamic considerations show that \( \sigma_{lv} \) is equal to the change in Helmholtz free energy of the surface, per unit increase of interfacial surface area.

The shape of a liquid-vapor interface can be strongly affected by surface tension. The Laplace equation can be derived by force balance on the interface, and for liquid drops where the interface is characterized by two radii of curvature \( (r_1 \) and \( r_2 \)), results in the following expression relating pressure difference across the interface with the surface tension \( \sigma_{lv} \),

\[ P_1 - P_2 = \frac{\sigma_{lv}}{r} \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \]  

(33)

When spherical symmetry exists, \( r_1 = r_2 = r \), and the interfacial pressure difference is,

\[ P_1 - P_2 = \frac{2\sigma_{lv}}{r} \]  

(34)

The Laplace equation relates interfacial pressure difference, surface tension, and interfacial geometry and therefore can be utilized in conjunction with equations of hydrodynamics to determine the shape of liquid-vapor interfaces. Alternatively, in an equilibrium situation with negligible hydrostatic pressure, the Laplace equation directly gives the pressure difference between the two phases. Thus, we find that for spherical droplets of water (e.g., condensation drops in fog), the liquid pressure can be as much as 2–5 atmospheres greater than the surrounding air pressure (for drop diameters of 1–2 μm).

Our interest here is in dropwise condensation on solid surfaces, wherein liquid drops exist on solid surface in presence of the vapor phase. Zisman [56] and de Gennes [57] give good reviews of the fundamental physics for such 3-phase systems. A macroscopic view of the contact line, where the three phases are in contact, can be expressed in terms of the free energy per unit area of each interface, i.e., the interfacial tensions \( \sigma_{lv} \), \( \sigma_{sl} \), \( \sigma_{sv} \), for liquid/vapor, solid/liquid, solid/vapor, respectively. Young’s equation, derived from equilibrium force balance, relates the contact angle \( \theta \) to the three surface tensions (interfacial energies),

\[ \sigma_{lv} \cos \theta = \sigma_{sv} - \sigma_{sl} \]  

(35)

where the contact angle \( \theta \) is traditionally taken to be the angle between the tangent to the liquid/vapor interface and the solid surface, measured on the liquid side. From thermodynamic considerations, it can be shown (see Carey [52]) that the net change of total system free energy per unit increase of solid/liquid interface area, for constant liquid volume and temperature, is

\[ \frac{\partial F}{\partial A_{sl}} = [\sigma_{lv} \cos \theta - \sigma_{sv} + \sigma_{sl}] \]  

(36)

and at equilibrium, total free energy is at minimum,

\[ \frac{\partial F}{\partial A_{sl}} = [\sigma_{lv} \cos \theta - \sigma_{sv} + \sigma_{sl}] = 0 \]  

(37)

which gives us Eq. (35) again. It should be noted that Young’s equation is an approximation that neglects:

- adsorption of fluid molecules on the solid surface
- variation of interfacial tension in local vicinity of the contact line
- dynamic effects in nonequilibrium situations.

The reader is referred to Johnson [58] for a detailed discussion of Young’s equation and its limitations. Wayner [59] also gives an excellent review of this topic, with special attention on physics of the contact line region.

In spite of its approximate nature, Young’s equation is a useful concept as we consider the phenomenon of wetting. A liquid is said to be wetting if it tends to spread as a film along the solid surface, and conversely to be nonwetting if it tends to retract and form “beads” on that surface. Force balance shows that if,

\[ \frac{\sigma_{lv} - \sigma_{sl}}{\sigma_{lv}} > 1 \]  

the contact line tends to pull away from the liquid bulk, thus spreading the liquid on the solid surface. Conversely, forced balance tends to pull the contact line inward toward the liquid bulk (beading) when,

\[ \frac{\sigma_{sv} - \sigma_{sl}}{\sigma_{lv}} < 1. \]  

(39)

Thus, Eq. (35) shows that wetting cases correspond to \( 0 \leq \theta < \pi/2 \). Conversely, nonwetting cases correspond to \( \pi/2 < \theta \leq \pi \). A spreading coefficient may be defined as,

\[ S_p = \frac{\sigma_{lv} - \sigma_{sl}}{\sigma_{sv}} \]  

(40)

A positive value of \( S_p \) corresponds to a net decrease of free energy per unit increase of solid/liquid interfacial area, necessary for spontaneous spreading of the liquid on the solid as clearly seen from Eq. (36) for case of \( \theta = 0 \).

Equation (40) indicates that solids with high surface energies \( (\sigma_{sv} > 100 \text{ ergs/cm}^2) \) tend to be more easily wetted. Indeed, most molecular liquids achieve good wetting on high-energy surfaces. Low energy surfaces \( (\sigma_{sv} < 100 \text{ ergs/cm}^2) \) can be wetted, partially wetted, or nonwetted, depending on the liquid specie (see de Gennes [57]). Figure 15 illustrates how the equilibrium contact angle \( \theta \) varies on a smooth Teflon (polytetrafluoroethylene) surface with the interfacial free energy \( (\sigma_{sv}) \) of n-alkane liquids. Clearly, the specific pairing of a liquid with a solid defines the balance between surface energies and thus the degree of wetting that can be obtained. For condensation, this balance governs whether filmwise or dropwise condensation is obtained. At the conditions represented by data points of Fig. 15, partial wetting is indicated and it is likely that condensation of these n-alkanes on the Teflon surface would occur in filmwise fashion, with some minimum film thickness, below which droplet/riblet formation occurs. The situation is notably different for water with its high interfacial energy \( (59 \times 10^{-3} \text{ N/m at normal boiling point}) \); the spreading coefficient \( S_p \) would be negative and one expects condensation to occur in dropwise fashion on this Teflon surface.
All these methods utilize reduction of the solid surface energy to obtain negative spreading coefficient have been employed for such purpose as, of surface energies. Tanasawa [60] classified the methods that have been employed for such purpose as,

1. Adsorption of a nonwetting agent (i.e., organic molecules) on condensing surface prior to operation.
2. Intermittent injection of nonwetting agent into the condensing vapor, for adsorption onto the condensing surface.
3. Plating the condensing surface with noble metal.
4. Coating the condensing surface with layer of organic polymer.

All these methods utilize reduction of the solid surface energy \( \sigma_{sv} \) to obtain negative spreading coefficient \( \delta_p \). It may seem that the plating of noble metals is an exception, in view of the high energies of pure metal surfaces. However, since elecrotplated surfaces of noble metals (e.g., gold, silver) are known to be highly active in adsorption of trace organic compounds, it has been suggested that it is the adsorbed organics that actually cause lowering of surface energy on the noble metal plating and promote dropwise condensation (see Wilkins et al. [61], Woodruff and Westwater [62]).

The use of coatings on the condensing surface must overcome three potentially detrimental problems. The additional thermal resistance through the thickness of the coating may negate any potential gain from dropwise condensation. This is of importance for coatings of low thermal conductivity, the case for most organic materials. In practice this limits the thickness of organic coatings to a few microns or less. Second, the bond between coating and substrate must be intimate so as to avoid a contact resistance for conduction across the bonding interface. Finally, for practical operation over long times, it is necessary for the coating to be robust mechanically and stable chemically. Marto et al. [41] evaluated several different coatings for sustained dropwise condensation of steam and found that the durability of organic coatings depended not only on the molecular structure and thickness of the organic material, but was also affected by the chemical activity and surface roughness of the solid substrate. These investigators reported organic coatings of fluoroacrylic on Ti/Au surface and of parylene-D on Cu/Ni surface that sustained dropwise condensation for periods exceeding 12,000 hours. An example of their data is shown in Fig. 12, indicating dropwise condensation coefficients of order \( 3 \times 10^4 \) W/m\(^2\)K. Low energy coatings can be applied by various techniques, with varying degrees of success in achieving low thickness, durability, and good bonding to substrate. One intriguing technique, using ion implantation, has been reported by D. C. Zhang et al. [63], and Q. Zhao et al. [64]. As described by Zhao et al., a copper substrate surface was deoxidized and then cleaned by sputtering in an \( \text{Ar}^+ \) beam. To develop a nonwetting surface, the clean Cu surface was then plated successively by ion implantation of Cr and N. Spectroscopic examination of the resulting surface showed an alloy layer with approximately 12% and 9% Cr and N content, respectively, along with noticeable amounts of C and O. Metalographic examination of the layer showed that the normal crystalline structure of Cu had been transformed into an amorphous state, with accompanying reduction of \(~30\%\) in elasticity. Since surface energy varies directly with modulus of elasticity, the new surface was of reduced surface energy. Because the low-energy layer thus obtained had thickness of \(<10^4\) Angstroms (\(<1\) \(\mu\)m), its conduction resistance was negligible and the investigators were able to achieve dropwise condensation coefficients up to \(3 \times 10^5\) W/m\(^2\)K on a vertical surface. In tests with steam condensing on treated copper tubes (vertical placement), the authors reported sustained operation for over a year. Ma et al. [65] subsequently coated polymers (polyhexafluoropropene and polytetrafluoroethylene) on brass surfaces by both ion-beam implantation and by plasma polymerization. While dropwise condensation was achieved with high heat transfer coefficients, these investigators concluded that the properties and durability of these coatings were sensitive to deposition process conditions (e.g., energy level of ion beam), and further study was recommended.

The current status for dropwise condensation may be characterized as a general acknowledgment that surface energy parameters are the governing keys, and that the ability to manipulate these parameter will determine successful applications of this mode of multiphase heat transfer in the future.

3.4 Further Developments. We next examine two fairly recent developments in manipulation of surface energies that are intriguing for dropwise condensation. Both developments are based on chemosorption, the modification of the solid surface energy, by use of self-assembled monolayers (SAMs) of organic molecules.

Certain organic compounds have terminal groups at the two ends of the molecule with very different chemical characteristics. For example, alkylthiol molecules have one end terminating with a HS group, the other end terminating with a CH\(_n\) group. The HS group can strongly bond with metal atoms of the solid surfaces, permitting good adherence of the organic molecule to the surface. The attached molecules then self assemble into a monolayer with the CH\(_n\) group sticking up over the surface, as illustrated in Fig. 16. By judicious choice of the terminal hydrocarbon group, different levels of surface energy can be obtained, hence controlling wetting characteristic of the solid surface. Because the self-assembled monolayers have thickness of order 10 angstroms, they present negligible resistance to heat conduction. Thus, the use of self-assembled monolayers promises to overcome the three potentially detrimental problems mentioned above.

Kumar and Whitesides [66] used SAMs of functionalized al-
Phobic and hydrophilic regions. Hexadecanethiol (HS(CH\(_2\))\(_{15}\)CH\(_3\)) with methyl termination, formed hydrophobic SAM regions, while 11-mercaptoundecanol (HS(CH\(_2\))\(_{11}\)OH), with hydroxyl termination, formed hydrophilic SAM regions. Condensation of water then occurred preferentially on the hydrophilic regions, generating diffraction patterns as desired by these investigators. Figure 17 (modified from their paper) illustrates the process of dropwise condensation progressing from a bare SAM covered surface, to initial formation of a few drops on some of the hydrophilic regions, to many uniform drops over all the hydrophilic regions, before eventually obtaining large drops that bridged over the hydrophobic regions to cover the entire surface. For the purpose of these investigators, it was particularly meaningful that micro-patterns of only micron length scale could be fabricated with such distinct regions of surface energies.

Das et al. [67] used an organic self-assembled monolayer coating to promote dropwise condensation of steam on a horizontal tube. SAM coatings of hexadecanethiol [HS(CH\(_2\))\(_{15}\)CH\(_3\)] were formed on copper, copper-nickel, and gold-coated aluminum tubes to obtain hydrophobic surfaces. The investigators reported that the coated surfaces had large advancing contact angles of 110–112 deg, reflecting their very low surface energies. The tubes were individually mounted in the apparatus shown in Fig. 18, and condensing heat transfer coefficients obtained by the Wilson plot technique. Some of their results for condensation of steam at sub-atmospheric pressure (10 kPA) are replotted in Fig. 19, along with the corresponding values for condensation on a bare tube (without SAM coating). It is seen that the heat transfer coefficients for SAM coated tubes were greater than those for the bare, uncoated tube of gold covered aluminum. Filmwise condensation coefficients, represented by the Nusselt theory (Eq. 18), are the smallest of all, being a factor of ~3 less than the coefficients for the bare tube. This implied that the gold-on-aluminum surface of the bare tube did obtain at least partial dropwise condensation. For the three SAM coated surfaces, the authors noted that thermal conductivity of the substrate material apparently had significant effect on the condensing heat transfer coefficient. This is contrary to the earlier results of Marto et al. [41], reproduced in Fig. 12, which indicated insensitivity to substrate material. Thus, the importance of constrictive thermal impedance in the substrate material remains an unsettled issue. For our purpose, the significant finding by Das et al. [67] is proof that self-assembled monolayers of organic compounds can be used to effectively promote dropwise condensation.

The second development of interest addresses the question, “can manipulation of parameters in the domain of surface energies not only promote dropwise condensation, but further enhance the heat transfer coefficient during dropwise condensation?” In seeking enhancement, one objective to explore is the control of drop size distribution and population density. As noted above and illustrated in Fig. 13, small drops are more effective than large drops in dropwise condensation. Graham and Griffith [47] estimated the fraction of heat flux due to drops of different diameters, plotting their results for various population distributions. Figure 20, reproduced from their paper (distribution numbers represent various assumed population distributions), indicates that the cumulative heat flux due to drops with diameter greater than 10 microns account for less than 35% of the total heat flux. This same indication of the importance of small drops is seen from the empirical correlation obtained by Tanasawa [60], reproduced here in Fig. 21. This plot shows a remarkably consistent correlation between average heat transfer coefficient and the diameter of departing drops. Since drops grow to largest size before departure, it is significant that reducing the diameter of departing drops from 2 mm to 0.2 mm increases the average heat transfer coefficient by almost 100%. Tanasawa’s plot further indicates that this enhancement is independent of the method for drop removal. The data of Fig. 21 included experimental data of constrictive thermal impedance in the substrate material.
ments using vertical gravitational force, inclined gravitational force, centrifugal force, and vapor shear to induce drop removal. It appears that the primary need is to remove drops from the condensing surface as early as possible during the drops’ growth cycle, by any means possible.

The work of Chaudhury and Whiteside [68] promises a novel development for promoting drop movement. They were able to induce drop movement uphill along a 15° incline by application of surface forces. Specifically, these investigators modified a method developed by Elwing et al. [69] to create a gradient of surface energy on the solid surface. A silicone wafer was exposed to a diffusing vapor of decyltrichlorosilane (Cl3Si(CH2)9CH3), which then chemically bonded to the silicone surface as a self assembled monolayer. Due to the concentration gradient associated with the diffusion process, the resulting SAM varied in concentration along the wafer, as illustrated in Fig. 22. Since the selected SAM had a hydrophobic terminal group, the free energy of the resulting surface varied with concentration, with lower values of \( \sigma_{sv} \) where SAM is more concentrated. These investigators reported that their SAM layer had a thickness of \( \approx 6 \) Angstroms at the hydrophobic end, decreasing at rate of \( \approx 1 \) Angstrom per mm toward the hydrophilic end. As illustrated in Fig. 22, the resulting surface had a gradient of surface energy, increasing along the wafer surface with increasing distance from the original source of silane. Figure 23, copied from Chaudhury and Whiteside [68], showed the static contact angle obtained for water drops at various positions along this gradient surface, varying over a range of almost 100 degrees.

A drop of liquid on a surface that has a spatial gradient of surface free energy would be subjected to unbalanced Young’s force. As illustrated in Fig. 24, for a cross-sectional slice of the drop of thickness \( dy \), the unbalanced Young’s forces is,

\[
dF_x = [\sigma_{sv} + \sigma_{sl}]_a - (\sigma_{sv} + \sigma_{sl})_b \, dy
\]
The net force on the drop is the integral of Eq. (41) over the thickness of the drop. This force can induce drop translation along the surface toward the region of higher surface energy. If the liquid/surface system has significant hysteresis, the net force would need to overcome the difference between advancing and receding contact angles to sustain drop motion. It is worth noting that such motion is not caused by classic Marangoni effect associated with concentration or temperature gradients in the liquid, but is strictly due to the unbalanced Young’s forces resulting from gradient in surface free energy. Chaudhury and Whiteside were able to obtain movement of 1–2 µm water drops, with average speed of 1 to 2 mm/s, upward on a surface inclined 15° from horizontal.

Leveraging from above finding, a project was initiated to determine if this phenomenon of unbalanced Young’s forces can be utilized to promote drop removal on condensing surfaces and thereby increase the condensation heat transfer coefficient. Figure 25 shows the test apparatus built for this experiment. A copper block of 5.0 cm diameter was sealed into a stainless steel vessel in such a manner as to create two separate chambers, each encompassing one surface of the copper block. Saturated steam was supplied to one chamber at controlled pressure and flow rate. Cooling water was sprayed onto the block surface in the second chamber. In operation, condensation occurs on the block surface in the steam chamber, the latent heat being conducted through the copper block to the water-cooled surface. The rate of condensation was adjusted by varying the rate of cooling water flow. During experiments, steam flow and cooling water flow would be maintained till steady state thermal conditions were obtained before taking measurements. To minimize non-condensable gases in the steam chamber, a continuous venting of excess steam was maintained during experiments. In selected tests, video records were obtained of the condensing surface to characterize the condensate removal process. Four microthermocouples were imbedded in the copper block to measure its temperature gradient, thus obtaining the heat flux through the block. Thermal insulation at sides of the block assured essentially one-dimensional conduction in the block, so that the heat flux obtained in the block represented the condensing heat flux \( q \) on the block surface. Extrapolation of the temperature profile to the condensing surface provided the surface temperature \( T_s \), while measurements of steam pressure and temperature provided the saturation steam temperature \( T_v \).

These measurements enabled direct calculation of the condensation coefficient as defined by Eq. (17), averaged over the circular condensing area of the block surface. Figure 26 shows an example of the temperature profiles measured in the copper block during condensation. The point plotted at each distance represents average temperature obtained in 16 measurements over an hour or more of operation. It is seen that a linear temperature profile was obtained, the correlation coefficient typically being greater than 0.99 (0.998 in case of the example in Fig. 26). Extrapolation of the temperature profile to surface of the condenser block and gradient of the profile provided quantitative values for wall surface temperature and heat flux, respectively, as indicated in the figure. This experimental apparatus was supported on a swivel such that tests could be performed with the condensing surface at various inclinations, from horizontal to vertical.

Using this apparatus, experiments were conducted in filmwise condensation, normal dropwise condensation and enhanced dropwise condensation (gradient surface). These different conditions were obtained by appropriate treatment of the condensing surface. In this paper, we will examine the results for filmwise and enhanced-dropwise condensation. For filmwise condensation, the copper surface was prepared by polishing to mirror finish, and then coated with a thin film (~ 10 Ågstrom thickness) of silicon by vacuum deposition. The silicon was then oxidized by exposure to a high temperature air, and plasma treated to remove all traces of adsorbed organic compounds. This resulted in a uniformly hydrophilic surface, upon which condensation occurred in filmwise fashion. For enhanced dropwise condensation, the silicon surface was subjected to a controlled silanization reaction by vapor diffusion, as illustrated in Fig. 22. Specifically, the silicon surface was first oxidized to SiO\(_2\), which was then reacted with a vapor of chlorosilane (Cl\(_3\)SiR), where the R group was a hydrocarbon chain of various molecular lengths. In presence of atmospheric water, the chlorosilane reacts with the SiO\(_2\) to form a series of silicon-oxygen bonds, thus creating a robust self-assembled monolayer film. Such SAM films have thickness of O[10 Ångstroms], and thus are of negligible thermal resistance. As noted above, the vapor diffusion process causes higher molecular concentration of the SAM on the regions of the surface in proximity to the chlorosilane source. By judicious placement of the source relative to the surface, we were able to produce various patterns of gradient energy on the condensing surface.

One pattern of particular interest was radial-centrosymmetric, with highest SAM concentration at the center of the circular condensing surface. This was produced by suspending the chlorosilane source at a point 2 mm above the Si surface, directly over the center point. The resulting SAM film had highest concentration at the center, the concentration decreasing with radial distance. To characterize the surface-energy landscape on this surface, static contact angles (with water) were measured at various radial posi-
larger drops, when compared to dropwise condensation on uni-
to midsize drops with a perceivable decrease in population of
such snapshots indicated a relative increase in population of small
down in the SAM coating process. Magnified observations from
paths was a result of the radial pattern of surface energies laid
radial pattern of drops flow. Clearly, this pattern of radial flow
adequately document the motion of drops, it does indicate the
SAM coated gradient surface. While such a snapshot does not
from a video sequence, showing the condensate pattern on the
video movies. Figure 28 presents a single frame extracted
condensation.
ents in free energy can promote drop motion and removal during
premise—that unbalanced Young’s forces on surfaces with gradi-
This result provided qualitative verification of the starting
followed the radial pattern of the gradients in surface energy.
showed that drop removal on the gradient surfaces did indeed
negligible shear force to cause drop movement. The video records
with minimal steam flow over the condensing surface, there was
horizontally oriented condensing surface, filmwise condensation was obtained. The condensate collected as a film on the horizontal surface, reaching a steady-state thickness when overflow drainage at the rim edge balanced the rate of condensate formation. In contrast, condensation on the SAM coated surface was of dropwise fashion. As commonly observed in dropwise condensation, droplets nucleated on the subcooled surface, growing by mass addition from condensation until occurrence of drop removal. The unique feature recorded for dropwise condensation on our gradient surfaces was the nature of drop removal. In as much as the condensing surface was horizontal, there was no gravitational force to trigger drop removal. Also, with minimal steam flow over the condensing surface, there was negligible shear force to cause drop movement. The video records showed that drop removal on the gradient surfaces did indeed occur very efficiently, and that the flow pattern for the drops followed the radial pattern of the gradients in surface energy. This result provided qualitative verification of the starting premise—that unbalanced Young’s forces on surfaces with gradients in free energy can promote drop motion and removal during condensation.

The visual impression of this process can best be obtained from the video movies. Figure 28 presents a single frame extracted from a video sequence, showing the condensate pattern on the SAM coated gradient surface. While such a snapshot does not adequately document the motion of drops, it does indicate the radial pattern of drops flow. Clearly, this pattern of radial flow paths was a result of the radial pattern of surface energies laid down in the SAM coating process. Magnified observations from such snapshots indicated a relative increase in population of small to midsize drops with a perceivable decrease in population of larger drops, when compared to dropwise condensation on uni-
form surface with gravity induced drop removal (comparing Figs.
28 and 11). At least qualitatively, the gradient in surface energy appears to have induced early drop removal, as desired.

One result of these experiments was surprising, namely the speed with which drops moved on the gradient surfaces. Pretest expectation was for drops of ~0.5–1.0 mm diameter to translate on the gradient surface with velocity of O(1 mm/s), as reported by Chaudhury and Whiteside [68]. Video records in the present experiment enabled measurement of drop velocity. Figure 29 shows two frames of the video taken 1 millisecond apart. On these magnified images, it was possible to track individual drops. In Fig. 29, the drop identified with number (1) had a diameter of 0.5 mm, and translated a distance of 0.15 cm in this time span. Thus, the effective velocity for this drop was 1.5 m/s. Similar results

**Fig. 27** Static contact angles on a circular surface with radial gradient of surface free energies, from Daniel [70]: ● SAM with octyltrichlorosilane; and ○ SAM with dodecytrichlorosilane.

**Fig. 28** Drop removal pattern during condensation on SAM surface with radial gradient in surface free energies, from Daniel, Chaudhury and Chen [71].

**Fig. 29** Video sequence of drop movement on gradient surface in time span of 1 millisecond, from Daniel [70].
were obtained for other drops tracked by the videos. This thousand-fold increase in drop velocity over expectation was startling. It suggests greater promise for enhancement of condensation heat transfer than originally anticipated. It also raises an intriguing question—what is the mechanism that would induce drop motion of such velocity? A hint was found in the fact that this accelerated drop motion occurred only during active condensation. In a series of tests, it was observed that the accelerated drop motion slowed significantly when the source of steam was cut off, resuming when the steam source to the condenser was restarted. It appears that the mechanism for accelerated drop movement derives from interaction between the condensation process and the unbalanced Young’s forces, requiring simultaneous presence of both.

One possible mechanism postulated by the co-investigators is the interaction of drop-coalescence process with the unbalanced Young’s forces. Daniel et al. [71] point out that drops grow during dropwise condensation, and coalescence occurs when neighboring drops grow into contact. When two drops coalesce, the resulting final drop has center of mass located between the centers of the two original drops, which represent a net displacement of the original drops. On a surface with gradient of surface energy, the growth of a condensate drop favors the circumferential edge that is in contact with higher energy (more wettable) surface. The resulting coalescence process would preferentially favor that direction, thus accelerating the net movement in that direction. This postulated mechanism may be correct, but in opinion of the present author it needs further investigation before complete acceptance. The occurrence of rapid drop movement during condensation on a gradient surface is an open and intriguing phenomenological issue.

Without fully resolving the mechanism for rapid drop movement, the experiments of Daniel et al. [71] did provide the first direct proof of principle, that engineering of surface energy gradients can enhance the heat transfer coefficient in dropwise condensation. The most telling evidence is found in comparison of data for dropwise condensation on a gradient surface with data for filmwise condensation on a uniformly hydrophilic surface. Figure 30 plots the heat transfer coefficients for these two cases, both obtained for condensation of saturated steam at ~1 atmosphere pressure on horizontal, up-facing surfaces. Measurements were obtained over ranges of subcooled surface temperatures, 2 to 18°K for dropwise condensation and 2 to 33°K for filmwise condensation. A very obvious enhancement was obtained in the case of dropwise condensation on the gradient surface. At the lowest surface subcooling of 2°K, typical for many applications, the heat transfer coefficient on the gradient surface attained a magnitude of approximately 2–3 times at such subcoolings. The results shown in Fig. 30 indicate that the enhancement on gradient surfaces diminished at higher subcoolings, presumably caused by limits in drop-flow capacity relative to increasing heat flux and condensate formation rate. Nevertheless, even at a surface subcooling of 18°K, there was a 4-fold enhancement in the heat transfer coefficient.

We concluded that for dropwise condensation, the parameter domain of surface free energy is critical. The experiments described above take advantage of parameters in this domain, creating engineered surfaces with gradients in surface energy which were observed to promote drop removal at velocities of $O[1 \text{ m/s}]$, even on horizontal surfaces. While the mechanism for this high-velocity drop movement is an open phenomenological question, the results indicate very substantial enhancement of condensation heat transfer coefficient.

4 Conclusion

The complexities of multiphase heat transfer often can be isolated for engineering purposes by judicious recognition of surface contact parameters in selected domains. The two diverse examples presented above illustrate this point. One showed that heuristic knowledge of time-domain parameters for surface contacts can significantly improve predictions of heat transfer coefficients for surfaces immersed in bubbling fluidized beds. The second showed that manipulation of parameters in domain of surface free energies can be utilized to gain many-fold enhancements of heat transfer coefficients in dropwise condensation.

Nomenclature

\[ \begin{align*}
\Delta r & = \text{Archimedes number} \\
C_b & = \text{Correction factor for small } Fo \\
c_p & = \text{heat capacity} \\
D & = \text{diameter of tube or bed} \\
D & = \text{diameter of drop} \\
d_p & = \text{diameter of particle} \\
F & = \text{Volumetric interaction force between gas and particles} \\
Fo & = \text{Fourier modulus} \\
f & = \text{fraction of time in residence at surface} \\
g & = \text{gravitational acceleration} \\
h & = \text{heat transfer coefficient} \\
h_l & = \text{latent heat of condensation/vaporization} \\
I_i & = \text{moment of inertia of particle } i \\
k & = \text{thermal conductivity} \\
M & = \text{molecular weight} \\
m_i & = \text{mass of particle } i \\
n_i & = \text{distribution of drop sizes} \\
Nu & = \text{Nusselt number} \\
P & = \text{pressure} \\
q & = \text{heat flux} \\
r_e & = \text{parameter in Lennard-Jones potential} \\
Re_p & = \text{Reynolds number based on particle diameter} \\
Pr & = \text{Prandtl number} \\
Q_f & = \text{heat transfer rate to drop} \\
R & = \text{Universal gas constant} \\
r & = \text{radius of curvature} \\
S_i & = \text{spreading coefficient} \\
T & = \text{temperature} \\
U & = \text{superficial gas velocity} \\
U_{ml} & = \text{superficial gas velocity at minimum fluidization} \\
U & = \text{local velocity} \\
v_i & = \text{linear velocity of particle } i \\
x & = \text{distance from heat transfer surface} \\
\end{align*} \]

Greek Notation

\[ \begin{align*}
\alpha & = \text{thermal diffusivity} \\
\alpha & = \text{accommodation coefficient} \\
\varepsilon & = \text{void fraction} \\
\varepsilon & = \text{parameter in Lennard-Jones potential} \\
\end{align*} \]
Subscripts

- $f$ = Lennard-Jones potential
- $\tau_r$ = residence time of packets
- $\omega$ = rotational velocity of particle $i$
- $\xi$ = penetration depth

Subscripts

- $b$ = bubble
- $c$ = condensation
- $g$ = gas
- $i$ = interface transfer resistance
- $ic$ = interface curvature effect
- $k$ = conductive resistance in liquid drop
- $l$ = liquid
- $m$ = minimum diameter drop
- $p$ = particle packets
- $s$ = solid particles
- $sat$ = saturation state
- $v$ = vapor
- $w$ = wall surface
- $x$ = maximum diameter drop

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