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Particle-based food systems subject to lipid migration – A review of measurement, modelling, and mitigation approaches

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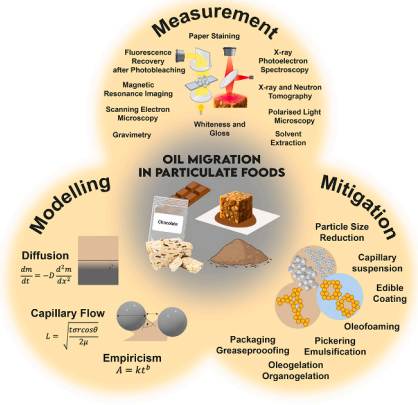
HIGHLIGHTS

- Two thirds of consumer foods are sold in particle-based forms and contain lipids.
- Oil, fat and grease are subject to migration within and out of the particle system.
- Lipid leaking results in quality defects on the food surface and the packaging.
- Modern migration measurement techniques, diffusion and capillary models are reviewed.
- Innovative oil stabilisation strategies for particulate foods types are discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

Many consumer food products such as confectionary or culinary seasonings are particle-based systems containing varying amounts of lipids such as oils, fats, and greases. Lipid migration is the result of inherent metastability of multiphasic particulate food systems. Lipid instability is further aggravated by climatic conditions, interaction with packaging, porosity, material transitions, and even gravity. Resulting lipid mobility can lead to various

Abbreviations: C, Carbon; CLSM, Confocal laser scanning microscope; CMC, Carboxy methyl cellulose; CPMG, Carr, Purcell, Meiboom and Gill sequence for NMR relaxometry; DAG, Diacylglycerides; EDX, Electron-dispersive x-ray spectroscopy; FID, Free induction decay; FMCG, Fast moving consumer goods; FOGs, Fats oils greases; FRAP, Fluorescence recovery after photobleaching; HOSO, High oleic sunflower oil; LSE, Least squares error; MAG, Monoacylglycerides; MRI, Magnetic resonance imaging; N, Nitrogen; NCT, Neutron computed tomography; NIR, Near infrared spectroscopy; NMR, Nuclear magnetic resonance; O, Oxygen; o/w, Oil-in-water; PFG-STE, Pulsed field gradient stimulated echo experiments for NMR diffusivity; PLM, Polarised light microscopy; RF, Radio frequency; RH, Relative humidity; *SCE*, Specular component excluded; *SCI*, Specular component included; SD, Standard deviation; SEM, Scanning electron microscopy; SFC, Solid fat content; *SG*, Surface gloss (−); SSE, Error sum of squares; T_2, NMR spin-spin relaxation time (s); TAG, Triacylglycerides; w/o, Water-in-oil; *WI*, Whiteness index (−); XCT, X-ray computed tomography.

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Food powders
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quality defects such as fat bloom on chocolate or oil stains on fibrous paper-based wrappers. This review revisits the factors influencing lipid migration and the generally accepted transport mechanisms diffusion and capillary flow. The most common measurement methods and modelling approaches described in the literature are discussed and assessed. Modern mitigation strategies to control lipid mobility are reviewed, with discussion on applicability to different particle-based food types and structures. Current trends towards healthier diets, clean-label recipes and sustainable packaging challenge traditional methods to stabilise lipids in food. As such a fundamental understanding, and measurement, modelling and mitigation strategies of lipid migration are highly relevant for a wide range of lipid-containing particulate foods.

Nomenclature

A	Migration cross sectional area (m^2)
A_{stain}	Oil stain area (m^2)
a^*	Colour space a-axis
b	Exponent (−)
b^*	Colour space b-axis
Bo	Bond number (−)
C	Mass fraction (kg kg^{-1})
C_∞	Equilibrium mass fraction (kg kg^{-1})
Ca	Capillary number (−)
D	Diffusivity (m^2 s^{-1})
D_{eff}	Effective diffusivity (m^2 s^{-1})
D_{50}	Median particle size (m)
d	Times (s)
d_p	Particle diameter (m)
E_{bind}	Electron binding energy (J)
E_{kin}	Electron kinetic energy (J)
G	Magnetic field gradient amplitude (T m^{-1})
g	Acceleration due to gravity (m s^{-2})
h	Jurin's height (m)
h_p	Planck's constant (J s)
I	Intensity (au)
I_0	Intensity at 0 T m^{-1} magnetic field gradient (au)
I_{int}	Integral spectral intensity (au)
i_ω	Intensity (au) at each Raman shift ω
J	Mass flux (kg m^2 s^{-1})
k	Rate constant (s^{-1})
k_b	Boltzmann's constant (J K^{-1})
k_c	Crystallisation rate constant (s^{-1})
k_m	Oil migration rate constant (kg $s^{-0.5}$)
k_s	Dissolution rate constant (s^{-1})
L	Capillary length (m)
l	Food body length (m)
L^*	Lightness (−)
m	Mass concentration (kg m^{-3})
M	Oil mass (kg)
M_∞	Equilibrium oil mass (kg)
M_t	Oil mass at time t (kg)
n	Number of terms (−)
P_{gas}	Gas-side pressure (Pa)
P_{liq}	Liquid-side pressure (Pa)
R^2	Correlation coefficient (−)
r_{cap}	Capillary radius (m)
r_{eff}	Effective radius (m)
r_m	Molecular radius (m)
r_{men}	Meniscus radius (m)
T	Temperature (K)
t	Time (s)
t_0	Midpoint time (s)
$t_{1/2}$	Recovery half-time (s)
v	Flow velocity (m s^{-1})
w	Bleached area radius (m)
x	Migration distance (m)
β	Avrami index (−)
γ	Gyromagnetic ratio (−)
Δ	Diffusion time (s)
ΔP	Pressure difference (Pa)
δ	Pulse duration (s)
ϵ	Voidage (−)
θ	Contact angle (°)
μ	Viscosity (Pa s)
σ	Surface tension (N m^{-1})
ρ	Oil density (kg m^{-3})
τ	Tortuosity (−)
ν	Frequency (Hz)
ω	Raman shift (cm^{-1})
ω_0	Lower spectral limits ($cm^{-1)}$
ω_n	Upper spectral limits (cm^{-1})

1. Introduction

An estimated 70% of all dry fast moving consumer goods (FMCG) for humans and pets are sold in particulate form, either as powders, granules, tablets, or particle-based dispersions [1]. A significant proportion of FMCG contain oils, greases, or fats added for food texturing, mouthfeel, flavour enhancement, health benefits from addition of essential oils, for purposely increasing calorific energy content, or for technical reasons such as dust control during manufacturing [2].

Generally, fats, oils, and greases (FOGs), amongst other components like lecithins, are classified as lipids. Oils are usually considered liquid at room temperature, whereas fats are solid, although many exceptions exists and thus a distinction based on their structure is more helpful. Fatty acids are aliphatic carboxylic acids and can contain from 4 to 24 carbon atoms in foodstuffs. Melting points for fully saturated fatty acids range from about 0 to 90 °C, whereas their unsaturated homologues do not tend to exceed 70 °C in melting temperature, owing to the alkene group. The absence of double bonds in saturated fatty acids generally results in a crystalline packing arrangement upon solidification, whereas in unsaturated structures the packing is less efficient due to the non-linearity induced by the double-bond, especially in the *cis* configuration [2].

When fatty acids are esterified with glycerol, mono-, di-, or triacyl glycerides (MAG, DAG, TAG) are formed, that solidify at room temperature. A given TAG molecule can crystallise in different polymorphs which bear different stabilities and thus melting points [2].

Greases are generally considered a biphasic mixture of liquid oil dispersed in a stabilising gelator matrix such as fats or waxes [3]. In particulate food systems, the lipid phase is essentially dispersed and in direct contact between particles, which for food products generally consist of crystalline or amorphous material. Crystalline particles are

generally inert to oil and humidity below their critical relative humidity (RH) due to their rigid crystal structure, but undergo deliquescence at higher atmospheric water content (75 %RH for table salt, 85 %RH for sucrose) [4]. Amorphous materials do not have a characteristic point beyond which they absorb water. Instead they gradually take up water and undergo sintering at rising environmental humidity due to an increase in free volume as small molecules such as water mobilise clusters of molecules [5]. Accordingly, various physicochemical phenomena in the lipid, crystalline, and amorphous phase can induce mobility of the lipid phase within, and out of the particulate food structure to its surrounding packaging. This metastability often referred to as fat, oil, or grease migration, release, or leaking [6], has serious implications for consumers and manufacturers alike, such as in fat bloom in chocolate confectionary [7–10] or in grease proofness of food packaging [11,12].

One of many consequences, oil leaking out of its protective food matrix is exposed to the oxygen containing environment and more prone to oxidation, responsible for the rancid off-flavour influencing taste perception of consumers [13]. For example, fat oxidation in dried dairy powder beverages is the main reason for rancid taste [14] and increase of surface fat is known to enhance powder caking and impede conveying, dispensing, and dissolution in manufacturing and vending settings [15].

Chocolate is also considered a particulate system majoritarily consisting of sugar and cocoa powder dispersed in a continuous cocoa butter or other fat matrix. Notorious fat bloom on chocolate implies a reduced quality in consumer preference [16,17] and it has been shown that visual opinionation influences taste perception of confectionary products [18]. Beyond organoleptic and hedonistic effects, hardness of chocolate has been shown to reduce as a result of oil migration due to lack of oil acting as a plasticizer, rendering the chocolate more brittle [19].

With the rising trend in food packaging paperisation, further technical implications on barrier properties are increasingly gaining importance. Paper and other fibrous packaging are porous media and thus generally have high affinity towards oils and greases compared to conventional packaging such as plastic, metal, or glass [20–22]. Fibrous packaging is thus more prone to lipid imbibition producing undesired visible stains on the exterior side of packaging. Visual packaging defects are a major reason for consumers rejecting food products, associating packaging damage with qualitatively inferior food [23]. Additionally, it has been shown that oils migrating into printed paper or cardboard can dissolve petrochemical-based inks and other oleosoluble coatings and contaminants, potentially entering into contact with food [24,25].

Other challenges within oil migration stem from current consumer trends in FMCG such as healthy diets, sustainable packaging, and shelf-life extension to reduce food waste. Classical approaches to prevent oil migration have been based on chemical transformations such as hydrogenation or interesterification that lead to higher fat viscosity at ambient temperature or fat crystallisation, thus rendering the lipid phase immobile. Substitution of fully saturated hard fats with unmodified (poly)unsaturated oils for health benefits results in a less viscous lipid phase, thus being more mobile to conditions driving oil migration [26,27]. Similarly, incorporating less processed but more whole foods into food structures means less structural modifications of the food microstructure for oil stabilisation can be undertaken [28,29]. Lastly, manufacturers' clean-label policies and legislative frameworks restrict certain additives in oil retention strategies [30]. For example, a clean-label approach would avoid artificial amphiphilic emulsifiers such as polysorbates and instead favour natural lecithin-based ones, that can however be less effective in lipid stabilisation [31] and allergenic due to residues from the plant they were derived from. In terms of packaging, comparisons of surveys show consumers rate paper as the most sustainable packaging type over plastic, metal, and glass [32–34], for which oil imbibition into its fibrous structure remains a challenge for oil migration control due to paper's strong capillary driven imbibition.

It is clear that lipid migration in particulate foods is a major quality concern in human and petfood alike. A fundamental understanding, and measurement, modelling and mitigation strategies are thus timely and relevant in the face of challenging consumer preferences on food and packaging. After having set out the motivation for oil migration control in particulate foods, this review revisits the current understanding of oil migration in particulate food systems (section 2), before describing recent measurement techniques (section 3) and modelling approaches (section 4) and discussing modern advances in mitigation strategies (section 5).

2. Oil migration in particulate food systems

As most multiphasic materials derived from nature that consist of more than a single pure compound, food containing particles and lipids is inherently thermodynamically metastable. The instability arises from concentration gradients due to localised concentration of material (e.g. liquid oil dispersed a fat matrix), due to pressure gradients (e.g. air in capillaries), or due to surface energy differences (e.g. small particles with large surface area) [35]. Kinetic constraints prevent the food from destabilisation immediately after preparation and in fact thermodynamic equilibrium is rarely reached [36]. Yet, microstructural and external phenomena such climatic conditions, interaction with packaging, porosity changes, material transitions, and even gravity can accelerate the destabilisation kinetics and result in enhanced mobility of the lipid phase. Lipid migration has generally been accepted to occur via three main routes: diffusion, capillary flow, or advection (convective mass transfer), whereby multiple processes are possible in the same system due to the typical complex structure of particulate food systems [8]. Lipid migration then manifests itself in various forms such as white fat bloom on chocolate, glossy greasy surface as in seasoning cubes, or oil stains on pet food paper packaging, besides secondary organoleptic effects as rancidity and reverse migration of packaging components into food [8,24,25,37,38].

2.1. Metastability

Metastability in particulate lipidous foods arises because the thermodynamic drive towards equilibrium and phase separation is slowed via kinetic effects [36]. Yet, mobile lipid fractions are subject to migration, of which several mass transport mechanisms are possible, either acting individually or combined.

Oils and fats are influenced by temperature and heat transfer between the environmental temperature and the food product, as for many fats used in foods the melting point is in the range of the ambient temperature on the planet and of the human mouth. With increasing temperature, oils become less viscous and more mobile, thus flow easier through a particle system and may be subjected to diffusion, capillary flow or advective flow [8]. Fats are generally composed of a mixture of multiple triacylglycerides and melt gradually from entirely solid to entirely liquid upon heating, with the range characterised by the solid fat content (SFC). Thus, increasing temperature increases the liquid fraction of the fat and its mobility for fat migration. Many fats exist in multiple polymorphic forms that can be achieved via controlled cooling or tempering from an initial molten state, and enhanced by seeding of the liquid fat with solid fat particles [39]. For cocoa butter triacylglycerides in chocolate for instance, six forms have been identified with different physical characteristics. Forms I to IV have the looser double chain packing, whereas forms *V* and VI have a denser triple chain packing, which also have a higher SFC at a given temperature, compared to looser less stable polymorphs [8,9]. Eutectic fat mixtures are mixtures of two or more fats that show incompatibilities between different fat phases and de-mix or segregate. This phase separation can cause fat migration by freeing the mobile fraction from a binding interaction with the less mobile fraction [40]. Multiple studies directly correlate viscosity, SFC and polymorph structures of cocoa butter and other fats with migration phenomena in chocolate [8,9].

Filled confectionary systems differ from the above single fat phase

systems by containing a core rich in liquid oils, such as cream, ganache, wafers or nuts, enrobed with a chocolate shell, that in itself contains a continuous fat phase. While there is evidence of fat migration leading to surface bloom in single triacylglyceride fat phase chocolate [41], most research focusses on oil-induced fat bloom. The suggested mechanisms inducing metastability are a dissolution of triacylglycerides in oil at the filling-chocolate interface, and diffusive transport of oil and triacylglycerides to the chocolate surface, driven by the concentration gradient between the oil-poor chocolate surface and oil-rich filling. Recrystallisation of triacylglycerides then occurs at the surface completing the migration pathway [42].

Many particulate food systems also occur as emulsions, either water-in-oil (w/o) or the reverse (o/w), or oil entrapped in fat. Metastability here is mostly induced by surface energy effects and insufficient interfacial stability between segregated phases. In emulsions, Ostwald ripening causes larger droplets or particles to grow at the expense of smaller ones [43], which in extreme cases leads to phase separation and thus frees any previously emulsified and stabilised phase to migrate, possibly via diffusion or capillary migrative flow. Similarly, in solid-liquid food systems such as chocolate, solid crystalline and amorphous particles can aggregate either due to moisture forming solid bridges between crystalline particles upon dissolution-recrystallisation, or due to sinter bridges between amorphous particles upon sintering [5]. While entrapment of oil into porous cocoa agglomerates seems plausible, hypotheses of pressure gradients for example induced by particle aggregation and oil displacement, leading to advective oil migration have also been proposed [10].

2.2. Diffusivity

Diffusion is defined as the transport of molecules of a mobile primary phase through a continuous stationary secondary phase, macroscopically driven by a concentration gradient, and microscopically by Brownian motion [44]. It was formalised into Fick's law by first assuming a constant concentration gradient between the rich diffusant and the depleted stationary phase [45,46]. At any instant in time dt, the mass flux J (kg m^2 s^{-1}) in and out of the interfacial area A is proportional to $m(x-l)l$ and $m(x+l)l$ respectively, where m is the diffusant concentration (kg m^{-3}), x is the diffusion distance, and l is the length of the food body through which diffusion occurs (m). (Fig. 1). The net flux is the difference of the two

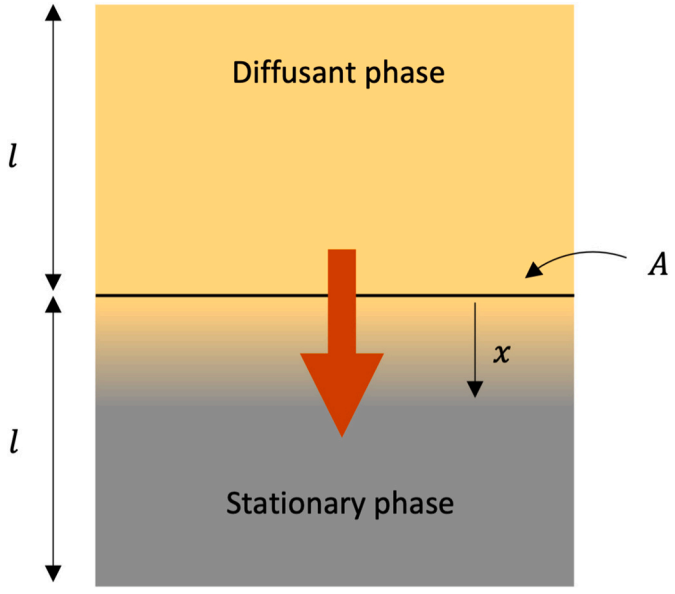

Fig. 1. Schematic of mass transport via diffusion.

$$J = m(x-l)l - m(x+l)l = m.x - ml^2 - m.x - ml^2 = -2ml^2 \quad (1)$$

However, m changes with location along the diffusing path, that is, there is a concentration gradient $m = \frac{dm}{dx}$. Hence,

$$J = -2l^2\frac{dm}{dx} = -D\frac{dm}{dx} \quad (2)$$

which is Fick's first law in 1 dimension for constant concentration gradient $\frac{dm}{dx}$ across the cross sectional area A. The diffusivity D absorbs $2l^2$ in a proportionality constant.

Diffusive migration of oil in most food products can be regarded as a batch process. This is because the amount of diffusant oil phase l and the size of the stationary phase l are limited, without constant influx or outflux. As a result, the concentration changes with distance x, yielding Fick's 2nd law

$$\frac{dm}{dt} = -D\frac{d^2m}{dx^2} \quad (3)$$

From the above derivation it follows, that the stationary phase needs to be permeable to the mobile phase. In particulate food products such as chocolate, the diffusion approach has been especially used to explain migration of oil through the fat phase, such as from an oil-rich filling or nuts through a chocolate coating to its surface, developing fat bloom. Explanations of fat permeability to oil have been proposed as a dissolution-recrystallisation or swelling process. In the dissolution-recrystallisation pathway, oil dissolves the fat upon its contact, allowing migration followed by recrystallisation and precipitation of the fat on the chocolate surface [42]. In the swelling mechanism, oil-induced imbibition of fat crystals and consecutive expansion increase the free volume in the fat matrix, allowing diffusive passage of oil, akin to moisture diffusion in polymer networks [47]. The free volume approach is supported for the chocolate system by the ability to reduce oil migration through the cocoa butter phase in chocolate by polymorph selection. Cocoa butter crystals of form I to I*V* are less dense owing to their double-chain structure compared to the denser triple-chain V and *VI* forms, resulting in less oil induced fat bloom. Additionally, D is affected by temperature as the thermal energy increases according to Einstein's relation $D = kT/6\pi\mu r_m$ where kT is the thermal energy (J), μ is the viscosity (Pa s) and r_m is the molecular radius (m) [48]. Generally, diffusion is considered a slow process compared to bulk flow of liquids via capillary action or advection [49].

2.3. Capillarity

While diffusion explains well transport in continuous biphasic systems, it does not fundamentally explain transport in triphasic solid-liquid-gas systems. Especially particulate food systems can contain porous voids either as interparticle or intraparticle space. For example, roasted cocoa particles contain up to 25 *v*/v% void space [50], while mercury porosimetry studies revealed a pore volume of up to 4 *v*/v% for chocolate overall [51]. An energy-dispersive x-ray spectroscopic study on fat migration in chocolate showed rapid oil transport that could not be explained by the slower diffusion time scales, but rather by taking into account the microstructural capillarity [52].

A liquid column held in a tube or particle system of sufficiently small diameter develops a meniscus and pressure gradient across the liquid/air interface, with high pressure on the air side and low pressure on the liquid side, given by the Young-Laplace equation [53,54].

$$P_{gas} - P_{liq} = \frac{2\sigma}{r_{men}} = \frac{2\sigma cos\theta}{r_{cap}} \quad (4)$$

where σ is the surface tension, r_{men} is the radius of the meniscus-tube curvature, and r_{cap} is the radius of a perfectly spherical capillary tube. In a monodispersely distributed spherical particle system (Fig. 2), an

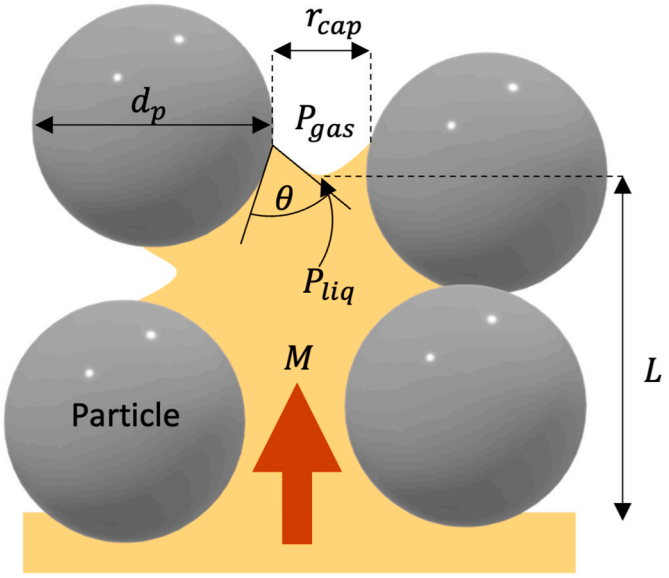

Fig. 2. Schematic of mass transport via capillary flow.

effective capillary radius r_{eff} (m) can be approximated by the voidage ϵ (−) and particle diameter d_p (m) [55,56].

$$r_{eff} = \frac{\epsilon d_p}{3(1-\epsilon)} \tag{5}$$

ϵ denotes the volume of space between particles that might for example, be filled by lipids or air. In real particulate food systems, measuring r_{eff} is challenging and requires advanced techniques such as gas adsorption or microtomography. In chocolate, pore diameters were estimated via atomic force microscopy to be 2 to 8 μm in diameter [57]. In a different study on chocolate employing synchrotron x-ray tomography, pore diameters of between 7 and 125 μm and several millimetre length were measured [58].

The pressure difference across the meniscus makes the liquid travel through the porous medium, in a vertical geometry until gravity balances the capillary suction, and in a horizontal or downwards flow until viscous forces balance. The maximum capillary rise h is given by Jurin's law [59,60].

$$h = \frac{2\sigma cos\theta}{\rho g r_{cap}} \tag{6}$$

where ρ is the liquid density, in the present case for example oil. Given that capillary rise is affected by gravity and viscosity, the question arises which force dominates. The transition from a capillary dominated to gravity controlled flow is suggested at a Bond number of $Bo = (2\rho g r_{cap})/\sigma = 1$; and similarly the switch from capillary controlled to viscous effects dominated flow is given as in the capillary number $Ca = \mu v/\sigma = 10^{-5}$, where v is the oil flow velocity [61,62]. In order to model the dynamics of liquid flow driven by the Laplace pressure, the flow regime is safely assumed to be laminar in the case of oil migration through food structures given the relatively long timescales required, and hence the Hagen-Poiseuille equation is applicable [63,64].

$$v = \frac{r_{cap}^2 \Delta P}{8\,\mu L} \tag{7}$$

Neglecting inertial and gravity forces, the pressure gradient is then replaced with the Laplace pressure, yielding the Washburn equation, linking the fluid flow distance with time, or mass transported with time [65].

$$L = \sqrt{\frac{t\sigma r_{cap} cos\theta}{2\,\mu}}, \text{ or } M = \rho\epsilon A\sqrt{\frac{t\sigma r_{cap} cos\theta}{2\,\mu}} \tag{8}$$

Because of the heterogenous nature of many porous media with different pore sizes, a combined mechanism for cellulose foams for example has been suggested to consist of fast initial capillary suction to reach Jurin's height, followed by slow diffusion. In such a system of parallel diffusion and capillary flow, the relative favour of capillary controlled flow over diffusion is generally given if the Péclet number $Pe = v\,L/D$ is larger than 1.0 [62].

3. Oil migration measurement in particulate food systems

The need to understand, predict, and mitigate oil migration and its adverse effects in particulate food systems has led to the development of multiple experimental monitoring techniques, illustrated in Fig. 3. They are direct measurements of oil migration such as the amount of oil released, the oil stain area on a contacting absorbing paper, or the amount of whiteness on a chocolate surface as a result of fat recrystallisation. In addition, the increased need to not only measure oil migration directly, but to also understand fundamental material properties, has led to additional measurement techniques that help understand microstructural metastability. While these techniques are indirect measurements of oil mobility, direct links between oil migration and for example differential thermograms, rheology, magnetic resonance, and x-ray scattering and diffraction patterns have been established. In the following sections, only key references are discussed to illustrate the different techniques but further examples of each measurement technique have been comprehensively tabulated in Table 1 in the same consecutive order.

3.1. Gravimetry

One of the most popular direct measurements of oil migration is the gravimetric weight determination of oil released (Fig. 3a). In order to measure the oil fraction migrated, the leaked oil needs to be separated from the food structure either in a filter paper or as the supernatant by centrifugation, and as such this technique is especially applicable to particulate food systems with high mobile oil fraction and permeable structures that leak oil fast, with rather capillary-controlled oil transport as opposed to diffusion. For example, multiple studies investigated formulation composition, amount of emulsifier, and the effect of edible fibre addition on oil release via gravimetry in the popular confectionary called halva [69]. As halva is made from sesame paste containing high amounts of liquid sesame oil in between sesame seed particles, oil migration into paper wrappers is of considerable concern in warm climate. To accelerate the gravimetric measurement, samples were centrifuged at up to 2000 g, allowing faster measurements. Centrifugation followed by gravimetry has also been used for ready-to-eat therapeutic food with high mobile oil fraction [72]. The disadvantage of centrifugation is that comparison with typical shelf-life conditions and packaging interactions is not possible, as normal gravity is only 1 g. Further examples are listed in Table 1.

3.2. Solvent extraction

Fats that are solid at room temperature don't readily flow into absorbing paper or phase-separate from the particle structure during centrifugation, and hence measuring oil migration is difficult, yet important. The fat migrating to the exterior surface in chocolate results in fat bloom, and fat migration into interparticle space of milk or cocoa powder causes caking, lumping, and poor reconstitution by rehydration and dissolution in water due to a hydrophobic fat layer. The fat contained in such particulate foods can be extracted by placing the sample into a bath of aliphatic or halogenated straight or cyclic hydrocarbons or

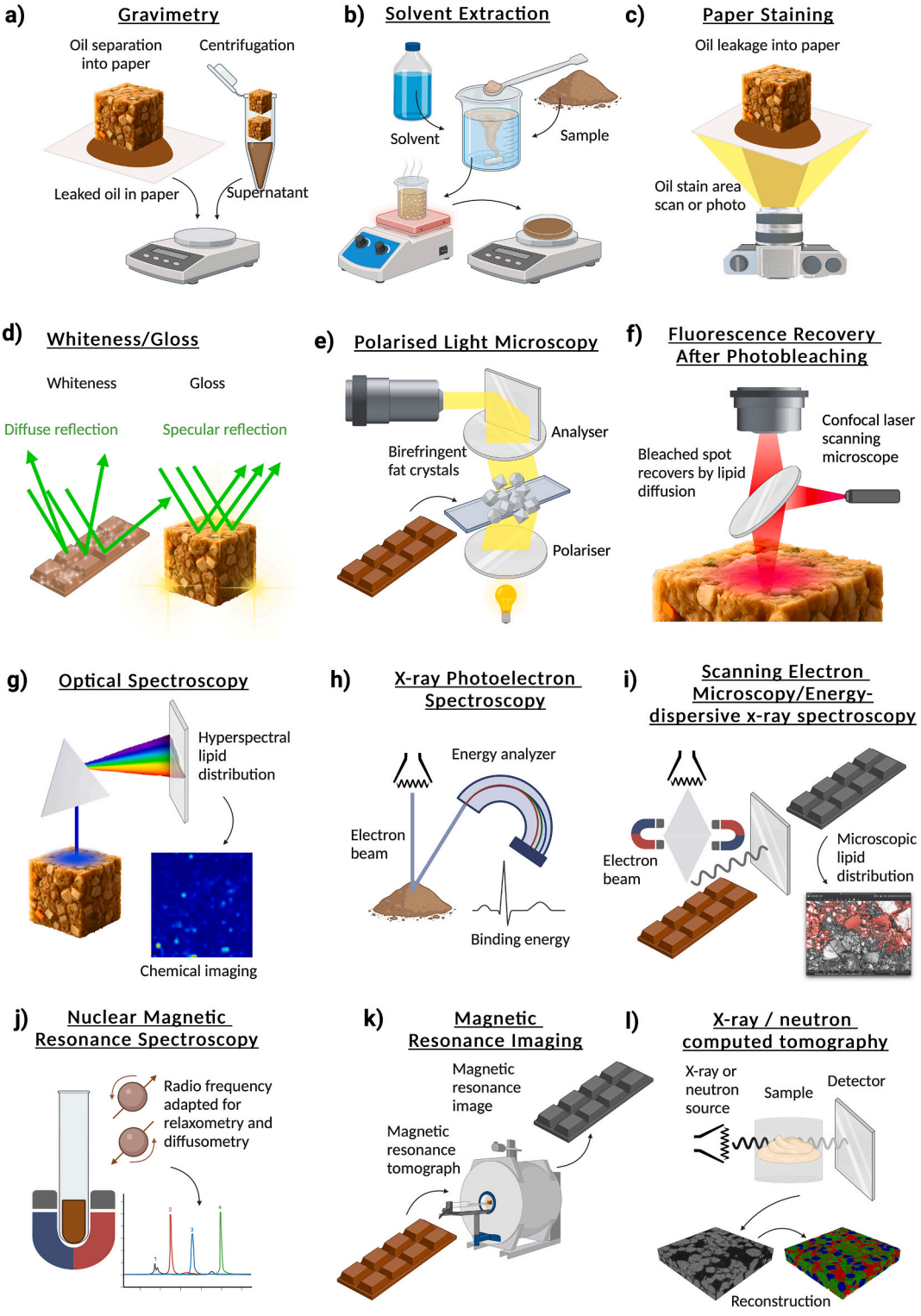

Fig. 3. Methods for measuring oil migration: a) gravimetry, b) solvent extraction, c) paper staining, d) whiteness and gloss, e) polarised light microscopy, f) fluorescence recovery after photobleaching, g) optical spectroscopy, h) x-ray photoelectron spectroscopy, i) scanning electron microscopy and energy-dispersive x-ray spectroscopy, j) nuclear magnetic resonance spectroscopy, k) magnetic resonance imaging, l) x-ray and neutron computed tomography.

alcohols (Fig. 3b). Gentle and short stirring at ambient temperature generally only dissolves surface free-fat, whereas the total fat content (surface and encapsulated) can be extracted by vigorous longer stirring at elevated temperatures [75]. The dissolved fat is then recovered gravimetrically after solvent evaporation. A clear separation of surface and encapsulated fats becomes difficult however with samples containing high porosity or prone to disintegration, and thus the protocol needs adjusting for different food materials. Jacquot et al. [73] and Petit et al. [74] used solvent extraction into petroleum ether for surface free and total fat quantification to evaluate fat migration in cocoa powder. Over 60 days at 20 and 40 °C, the surface free fat content increased from 6 to 9 *w*/w% of total cocoa powder mass, but still

Table 1
Common measurement techniques of oil migration in particulate food systems.

Measurement	Food material	Investigation	Ref
Gravimetric	Phytosterol-sunflower oil oleogel	Effect of phytostyrol/HOSO ratio on oil migration into paper substrate	[66]
	Fat blend (Saturated/unsaturated soybean oil)	Effect of fat/oil ration and emulsifier type on oil migration into paper substrate	[67]
	Halva (sesame paste, sugar, corn fibres)	Effect of emulsifiers and corn fibres on oil migration into filter paper by centrifugation	[68]
	Halva (sesame paste, sugar, sesame testae (sesame hull waste), date fibres)	Effect of emulsifiers, sesame testae and date fibres on oil migration into filter paper by centrifugation	[69]
	Halva (sesame paste, sugar, palm oil, citric acid, glycerol, CMC, gelatine etc)	Effect of additives on oil migration into paper substrate	[70]
	Halva (sesame paste, sugar)	Effect of type of emulsifier on oil migration into paper substrate	[71]
	Ready-to-use therapeutic food (ground peanuts, palm oil, soybean oil, sugar, milk, micronutrients, emulsifiers)	Effect of emulsifier type and quantity on oil release upon centrifugation	[72]
Solvent extraction	Cocoa powder	Effect of storage temperature on fat migration to surface	[73]
	Cocoa powder	Effect of cocoa type and storage temperature on fat migration into interparticle voids	[74]
	Skimmed, whole and cream milk powder	Effect of storage time on fat migration to particle surface	[75]
Optical oil stain area on paper	Model pet food (Silica gel and greases)	Grease release from pet food via oil stain extent on paper	[38]
	Palm kernel fat	Effect of high-intensity ultrasound on oil migration into paper	[76]
	Oleogel (rapeseed oil, Myverol, sunflower oil, candelila wax)	Oil migration from oleogel via growth of grease stain extent on paper	[77]
	Model stock cube (salt, sunflower oil)	Effect of crystalline phase particle size on oil migration via extent of oil stains on paper	[37]
Whiteness index and surface gloss	Fat blend (cocoa butter, tricaprylin, flaxseed oil, safflower oil, peanut oil)	Effect of oil viscosity on oil migration through fat matrix	[78]
	Dark chocolate (cocoa butter, cocoa, sucrose, lecithin, cocoa butter seeds)	Effect of tempering and seeding on fat migration to chocolate surface	[79]
	Chocolate-enrobed cream-filled wafer cookies	Effect of packaging wrapper on oil migration from cream filling to chocolate coating surface	[80]
	Dark chocolate (cocoa butter, cocoa, sucrose, lecithin)	Effect of sucrose particle size on fat migration to chocolate surface	[81]
	Dark chocolate (cocoa butter, cocoa, sucrose, lecithin)	Effect of phospholipid emulsifiers on fat migration to chocolate surface	[82]
	Chocolate (cocoa mass, cocoa butter seeds)	Effect of temperature cycling on fat migration to chocolate surface	[41]
	Dark chocolate (cocoa butter, palm fat, mango kernel fat)	Effect of physical blends and interesterification on surface fat crystallisation	[83]
	Model chocolate (cocoa butter, sand)	Effect of sand particle size on oil migration to chocolate surface	[84]
	Dark chocolate (cocoa butter, cocoa, sucrose, stearates)	Effect of stearate and storage conditions on oil migration to chocolate surface	[85]
	Chocolate filled with white chocolate ganache cream	Effect of storage pressure and temperature on oil migration from filling and into chocolate	[86]
	Chocolate (cocoa butter, cocoa nib, lecithin, sucrose, maltitol, tagatose)	Effect of sweetener on fat migration to surface	[87]
	Fat blend (soft palm mid fraction, high oleic sunflower oil)	Effect of liquid oil fraction on surface fat crystallisation	[88]
	Palm kernel fat	Effect of high-intensity ultrasound on surface fat crystallisation	[76]
	Chocolate (cocoa mass, cocoa butter seeds)	Effect of temperature cycling on surface fat crystallisation	[41]
	Dark chocolate (cocoa butter, palm fat, mango kernel fat)	Effect of physical blends and interesterification on surface fat crystallisation	[83]
Polarised light microscopy	Fat blend (palm/peanut oil layer on cocoa butter layer)	Effect of TAG composition on surface fat crystallisation	[89]
	Palm kernel fat/soybean fat blend with triolein	Effect of TAG/fat ratio on surface oil crystallisation	[90]
	Phytosterol-sunflower oil oleogel	Effect of phytosterol/HOSO ratio on surface oil crystallisation	[66]
	Cream filling (peanut oil, interesterified hydrogenated palm oil, lecithin, sugar), cocoa butter	Effect of cream filling composition (lecithin, sugar) and shear rate of shear-crystallised cocoa butter on surface fat crystallisation	[91]
	Chocolate (sugar, cocoa butter, cocoa)	Effect of pre-crystallisation and particle addition on oil diffusion	[92]
Fluorescence recovery after photobleaching	Fat blend (saturated/unsaturated canola oil)	Effect of SFC on oil diffusion through fat	[93]
	Fat blend (palm kernel fat, soybean fat, triolein)	Effect of TAG/fat ratio oil diffusion through fat	[90]
Optical spectroscopy	White chocolate	Surface composition and pore morphology of white chocolate linked to fat bloom	[94]
	Model stock cube (salt, sunflower oil)	Effect of crystalline phase particle size on oil migration via surface oil concentration chemical imaging	[37]

(*continued on next page*)

Table 1 (*continued*)

Measurement	Food material	Investigation	Ref
Scanning electron microscopy	Chocolate-enrobed cream-filled wafer cookies	Effect of packaging wrapper on oil migration from cream filling to chocolate coating surface	[80]
	Dark chocolate (cocoa butter, cocoa, sucrose, lecithin)	Effect of sucrose particle size on surface fat crystallisation	[81]
	Dark chocolate (cocoa butter, cocoa, sucrose, lecithin)	Effect of phospholipid emulsifiers on surface fat crystallisation	[82]
	Chocolate (cocoa mass, cocoa butter seeds)	Effect of temperature cycling on surface fat crystallisation	[41]
	Chocolate (cocoa butter, cocoa nib, lecithin, sucrose, maltitol, tagatose)	Effect of sweetener on fat migration to surface	[87]
	Silicone oil/canola oil impregnated cotton pad on chocolate	Effect of type of oil migration through chocolate to opposite side via EDX	[52]
	Chocolate (cocoa, cocoa butter, milk powder, sucrose)	Effect of tempering and storage conditions on fat migration to surface	[95]
X-ray photoelectron spectroscopy	Cocoa powder	Effect of storage temperature on fat migration to surface	[73]
	Cocoa powder	Effect of cocoa type and storage temperature on fat migration into interparticle voids	[74]
Nuclear magnetic resonance	Fat blend (soft palm mid fraction, high oleic sunflower oil)	Effect of liquid oil fraction on diffusion through fat matrix	[88]
	Oleogel (sunflower wax, hazelnut oil, MAG, DAG)	Effect of wax and emulsifiers on oil diffusion through olegoel	[96]
	Fat blend (tricastin and tristearin)	Effect of oil-gelator ratio and SFC on oil migration through fat blend	[97]
Magnetic resonance imaging	Fat blend (palm oil, peanut oil layer on cocoa butter)	Effect of TAG composition on oil migration through fat matrix	[89]
	Chocolate layer (cocoa liquor, cocoa butter, icing sugar, stevia, sucralose, maltodextrin) in contact with hazelnut paste	Effect of sugar and sweeteners combination on oil migration through chocolate layer	[98]
	Cream filling layer (hazelnut oil, interesterified hydrogenated palm oil, lecithin, sugar) on cocoa butter layer	Effect of cream filling composition (lecithin, sugar) and shear rate of shear-crystallised cocoa butter on oil migration through cocoa butter matrix	[91]
	Almond cream filling layer on dark chocolate layer	Effect of different almond filler formulations on diffusion through chocolate	[99,100]
X-ray and neutron computed tomography	Oleofoam from high oleic sunflower oil and cocoa butter	Effect of oleofoam formulation composition, whipping time, and storage time on bubble morphology via x-ray tomography	[101]
	Couscous grains exposed to high humidity environment	Effect of storage time and humid air flow rate on grain morphology via combined x-ray and neutron ray tomography	[102]
	Starch and spirulina extrudate	Effect of formulation composition on mechanical and morphological properties via neutron computed tomography	[103]

remaining below the total fat content of 10.5%, thus suggesting that 1.5 w/w% of fat remained encapsulated within the cocoa powder. Fat migration was more pronounced at elevated temperatures and resulted in increased unwanted powder caking, which is highly undesirable for beverages containing cocoa powder such as hot chocolate. Kim et al. [75] investigated fat migration in skimmed, whole, and cream milk powders with 1, 27, and 72 *w*/w% fat contents over 6 months. Surface free-fat was extracted with a brief hexane wash over filter paper, whereas total fat extraction was carried out with 50 °C water and hexane/isopropanol mixture for 30 min. It was found that surface free-fats almost doubled in percentage over the shelf-life period, highlighting that even fats solid at ambient temperature undergo significant migration dynamism. The works discussed are summarised in Table 1.

3.3. Paper staining

In the case of oil migration from particles structures into paper substrate, it was shown for model seasoning cubes that gravimetric measurements are equivalent to evaluation of oil stain area. This equivalence is given as long as the fibrous structure is isotropic and of constant thickness, as the volume of oil in the oil stain on paper is linearly related its mass by the oil density [37]. Due to this, monitoring oil migration into fibrous substrates by measuring oil stain area is an attractive technique to evaluate oil stability in contact with food packaging, especially with the increasing trend of packaging paperisation often resulting in porous fibrous materials in direct contact with foods (Fig. 3c). Notably oil migration measurements for greasy foods such as pet nutrition [38], stock cubes [37], or foods based on oil gels (oleogel) emulsions [3,77] have been reported by oil stain migration. Simple manual area estimation as well as sophisticated automated imaging via photography or scanning were employed. Because of refractive index matching of paper fibres and oil, light transmission of oil-imbibed paper is augmented in contrast to oil-free paper with more scattering, and thus resulting in different grey values [37]. By calibrating the ratio of pixel to actual distance on paper, the number of darker pixels can be thresholded and quantified in area units via an image analysis software such as imagej/fiji [104]. The observed elliptical elongation of oil stains on rolled paper is due to the fibre orientation along the machine direction during manufacturing, which can be circumvented by using pressed paper or blotting paper. Table 1 summarises the studies using paper staining measurements.

3.4. Whiteness and gloss

In particulate food systems with dense structures and little to no porosity, oil migration is slower and rather diffusion controlled and may involve other phenomena such as dissolution/recrystallisation, and hence gravimetric and paper substrate methods may not be useful. A prominent technique for such types of particulate foods like chocolate is measurement of the amount of white colour formed due to surface fat recrystallisation as a result of oil entrained migration (Fig. 3d). Compared to the smooth glossy surface of fresh chocolate, fat crystals deposits are coarse and rough, causing incident light diffraction into the

full spectrum leaving a white appearance on the chocolate surface. Spectrophotometry or colorimetry of chocolate samples is able to measure L^* a^* b^* as either specular reflectance included (*SCI*) and specular reflectance excluded (*SCE*), where L^* is the lightness, and a^* and b^* are the axes in the CIELAB colour space [105]. The white appearance on chocolate can then be expressed using the colour parameters as whiteness index, *WI* [106]

$$WI = 100 - \sqrt{\left(100 - L^*_{SCE}\right)^2 + \left(a^*_{SCE}\right)^2 + \left(b^*_{SCE}\right)^2} \quad (9)$$

Closely related to *WI* is the surface gloss, *SG*, defined as [107].

$$SG = \sqrt{\left(L^*_{SCE} - L^*_{SCI}\right)^2 + \left(a^*_{SCE} - a^*_{SCI}\right)^2 + \left(b^*_{SCE} - b^*_{SCI}\right)^2} \quad (10)$$

It is less prominent than WI but has been used alongside it to measure the decrease in surface glossiness as migrated fat crystals increasingly diffract light, hence *SG* showing an inverse trend to *WI* [79]. Further literature of particle systems, especially chocolate, employing whiteness measurements are summarised in Table 1.

3.5. Polarised light microscopy

Another measurement technique to assess fat crystallisation as a result of oil migration is polarised light microscopy (PLM) (Fig. 3e). It has been applied mostly qualitatively for crystallised cocoa fat blends [88] and chocolate containing crystalline sugar particles [91]. In this contrast enhancing technique, light is passed through a linearly polarising filter and then through the sample, which rotates the incident light depending on the extent of crystallisation. The light is recombined by a second polarising filter, creating an image where the birefringent nature of crystalline material allows passage of light as opposed to non-birefringent material, blocking the light leaving a black contrast. When analysing fat blends, crystalline sugar particles interfering with the fat crystals can be washed out with deionised water [83]. PLM is thus similar to WI as it allows measurement of surface fat crystallisation induced by oil migration, with the disadvantage of PLM to require thin samples to avoid visible light opacity. Also, during PLM the sample is sandwiched between two glass slides, which in most cases is different to the native state of the product. Further works employing PLM are listed in Table 1.

3.6. Fluorescence recovery after photobleaching

While the above optical methods allow to quantify surface effects of oil migration, it is also beneficial to measure mass transport properties to explain and model oil migration. An optical technique developed for this purpose is Fluorescence Recovery After Photobleaching (FRAP), within a Confocal Laser Scanning Microscope (CLSM) [108] (Fig. 3f). A dye that exhibits fluorescence when exposed to the laser wavelength of the CLSM is used as a tracing agent within the sample. A localised spot of the fluorophore on the sample surface is destroyed or bleached by a strong laser pulse, and the optical density during closure of the spot monitored. Closure of the patch depends on the mobility of the dye, which can be expressed by the formula developed for a Gaussian distribution of the bleaching laser beam, to account for diminished laser intensity towards the edges of the spot [108].

$$D = \frac{0.88w^2}{t_{1/2}} \quad (11)$$

where w is the bleached area radius, and $t_{1/2}$ the recovery half-time. FRAP has been used to measure diffusivity of oil during migration processes in particulate food samples. As listed in Table 1 for example, Svanberg et al. [92] used the fluorescent fatty acid BODYPY FL C_{16} as oil in model chocolate containing cocoa butter as the fat phase, cocoa and sugar particles. Diffusivities between 1×10^{-13} to 7×10^{-12} $m^2 s^{-1}$ were reported. Green and Rousseau [93] and Chai et al. [90] used lipophilic fluorchromes fluorofol yellow 088 and Nile Red mixed with the liquid fraction (canola oil, or triolein), in fat blends with saturated canola oil or saturated palm fat respectively as gelators, assuming that the dye migrates at the same rate as the oils, which is a reasonable assumption if molecule shape and molecular weight are similar. Measured diffusivities ranged from 1×10^{-13} to 1.5×10^{-11} $m^2 s^{-1}$. As all surface techniques, also CLSM and FRAP capture only surface phenomena, which may be different to the behaviour within a particulate system.

3.7. Optical spectroscopy

Besides photographic or spectrophotometric techniques, also optical spectroscopic methods for oil migration measurement have been reported, such as Raman and Near Infrared spectroscopy (Fig. 3g). Raman spectroscopy is a technique in which a monochromatic light, e.g., from a laser source, is shone on a specimen and the inelastic backscattering (stokes scattering) is quantified by counting the number of photons excited or absorbed in a charge-coupled device camera, expressed as intensity for a certain wavelength, customarily expressed as wavenumber (cm^{-1}). For a sample to exhibit a Raman effect, the molecules must be polarisable, which is generally the case in covalently bonded samples such as organics, but not in purely ionic species without shared electrons. It is thus possible to differentiate between organic and inorganic substances, as well as between multiple organic materials as different functional groups exhibit different Raman signatures. Near infrared techniques are similar to Raman with the difference that NIR cameras capture the infrared absorption, but similarly exhibit fingerprint regions with peaks characteristic of certain molecules. For analysis or imaging scenarios, it is generally aimed to identify non-overlapping spectral peaks for each material, which essentially depends on the resolution of the acquisition equipment. If peak separation is possible, integral intensity can be calculated as the area under the characteristic peak, approximated as [37].

$$I_{int} = \int_{\omega_0}^{\omega_n} i_\omega = \sum_{\omega_0}^{\omega_n} i_\omega \quad (12)$$

where I is the integral intensity (au), ω_0 and ω_n are the lower and upper spectral limits respectively (cm^{-1}), and i_ω is the intensity (au) at each Raman shift ω.When acquiring spectra not only at single point but in a 2D array, resolving the integral intensity in the x-y map can provide a visual representation of the sample's chemical nature as a chemical image, which is otherwise invisible to optical or photometric techniques. Both Raman and NIR spectroscopy have been applied for measurements of oil migration. In cream-filled wafer chocolate, Fourier transform NIR (FT-NIR) was used to obtain spectra of the chocolate surface under different packaging materials, enabling to link fat migration and bloom with packaging type and storage time [80]. Spatial Raman measurements were performed on white chocolate generating chemical images of the surface composition and fat distribution [94]. In a study on model stock cubes in contact with paper packaging, spatiotemporal Raman chemical imaging was performed rendering quantitative images of sunflower oil concentration at 1 day time intervals. Augmentation of chemical imaging by a time dimension allowed to visualise the oil dynamism on the food surface, which was not achieved previously [37].

3.8. X-ray photoelectron spectroscopy

Instead of using visible or infrared light, also x-rays can be used for spectroscopy. X-ray photoelectron spectroscopy (XPS) or electron spectroscopy for chemical analysis (ESCA) makes use of the photoelectric effect in which electrons are emitted from a sample due to incident x-rays of a fixed energy, for example 1486.7 eV for an *Al* Kα source [109] (Fig. 3h). If the binding energy E_{bind} holding the electrons with atoms in less than the incident energy $h\nu$ (where h is Planck's constant and ν the frequency), then the kinetic energy of the E_{kin} of the released electron

follows Einstein's photoelectric relation [110].

$$E_{kin} = h\nu - E_{bind} \quad (13)$$

By measuring E_{kin} for example via a hemispherical energy analyser, E_{bind} can be found and plotted against its detection intensity, yielding an XPS spectrum. E_{bind} is dependent on the atom itself and on neighbouring atoms that share valence electrons across covalent bonds. Thus, each atomic element and group of two to three bonded atoms has a characteristic E_{bind}, giving rise to fingerprint XPS spectra that can be used to determine surface composition, and thus also lipids. Due to x-rays finite energy the sampling depth is usually limited to 5–10 nm below the sample surface, and ultra-high vacuum is required to avoid interaction of x-rays with matter excluding the sample.

James and Smith [95] investigated fat bloom on chocolate surfaces as a result of fat migration and recrystallisation over 30 days for chocolate prepared under different tempering conditions. XPS profiles were generated for pure material based on the prominent covalent bonds in the material (e.g. O-C-O in sucrose, O=C-OH in cocoa butter), allowing to monitor the development of surface composition over time. This technique is however laborious for complex formulations as detailed preliminary information on the ingredients chemical structures is required. For particulate foods containing less complex compositions, simple aggregation of atoms is sufficient. For example, lipids have a relatively higher carbon © content than carbohydrates, which tend to contain more oxygen (O), whereas proteins are characterised by the presence of nitrogen (N). As such, the C/O ratio and percentage of N were used to characterise fat migration in different types of cocoa powder stored under temperatures of 20 to 40 °C [73,74]. Fat migration into interparticle spaces in cocoa, such as in powdered beverages, are major reasons for caking, visual quality defects, and difficult reconstitution. Over time, especially at higher storage temperatures, the XPS showed an increasing C/O ratio, whereas the surface N percentage decreased, as a result of fat gradually covering carbohydrate and protein areas on the cocoa particles. Increased powder caking was attributed to formation of interparticle fat bridges as a result of fat migration.

3.9. Scanning electron microscopy

Another classical surface characterisation technique applicable to oil migration measurements in particulate foods is scanning electron microscopy (SEM), in which an electron beam accelerated by a certain voltage and guided by an electromagnetic field is targeted at the surface of a bulk sample and the backscattered or secondary electrons detected (Fig. 3i). SEM can also be used to spatially map materials of different chemical natures by employment of energy-dispersive x-ray spectroscopy (EDX), in which photons of individual chemical elements are emitted at specific acceleration voltages, a process termed Bremsstrahlung. The characteristic peaks on an x-ray emission spectrum can thus be used to identify different materials based on key chemical elements contained within them, akin to chemical imaging with other spectroscopic methods. SEM has been employed to monitor surface fat crystallisation in chocolate as a result of oil migration, while EDX was used to identify the surface composition over time of a silicon enriched oil-filled chocolate sample during oil migration events [52]. While oil migration is usually considered a relatively slow diffusion driven process, spots of oil from the filling on the chocolate surface were identified surprisingly fast after preparation of the chocolate, which the authors attributed to capillary flow through or adjacent to porous cocoa particles. Table 1 lists further works employing SEM.

3.10. Nuclear magnetic resonance

While the adverse effects of oil migration such as fat bloom or grease-imbibed packaging are affecting the food surface, there is an increasing interest to measure and understand oil migration phenomena within particulate food structures. Thus, methods that not only probe the food surface but similarly the interior structure are necessary. Nuclear magnetic resonance has been used as a non-destructive technique in various experimental configurations to monitor various aspects of oil migration (Fig. 3j). Magnetic nuclei in molecules enter into resonance when subjected to strong electromagnetic fields, which's oscillation frequency can be measured to obtain spectra. In the simplest free induction decay (FID) setup, ^{1}H NMR spectra for different materials give rise to peaks at different chemical shifts, characteristic of the proton(s) in the analyte's functional groups, giving rise to a molecular fingerprint [88,96,97]. NMR relaxometry moves beyond mere analytical characterisation and enables estimation of molecular mobility based on the relaxation process to equilibrium. This transverse relaxation is commonly induced by sequencing the pulses of radio frequency (RF) in a multi echo sequence according to Carr, Purcell, Meiboom and Gill (CPMG) [111]. The measured spin-spin relaxation time, T_2, is linked to the molecular motion: large T_2 corresponds to fast molecular motion and short T_2 corresponds to slow molecular motion. NMR diffusometry allows quantitative evaluation of the mobility by expression as diffusivity, D, from pulsed field gradient stimulated echo experiments (PFG-STE). D is obtained from the Stejskal and Tanner equation [112].

$$\frac{I}{I_0} = exp\left(-\gamma^2 G^2 \delta^2 \left(\Delta - \frac{\delta}{3}\right) D\right) \quad (14)$$

where the signal intensity I at the magnetic field gradient amplitude $G = 0$ T m^{-1} is given by I_0, γ is the gyromagnetic ratio, δ the pulse duration, and Δ is the diffusion time. All three NMR techniques were used to measure liquid oil migration in solid fat matrices in fat blends or oleogels. Trapp et al. [96] analysed hazelnut oil-based oleogels with sunflower seed wax or mono- and diglycerides, the latter found in chocolate confectionary. First, FID was used to obtain NMR spectra for each raw component of the oleogel formulations, followed by relaxometry (CPMG) and diffusometry (PFG-STE). Adam-Berret el al. [97] and Nelis et al. [88] also applied the latter two techniques to tricaptrin and tristearin blends, and sunflower oil-palm fat mixtures respectively. Representations of I/I_0 against $-\gamma^2 G^2 \delta^2 (\Delta - \delta/3)$ in the Stejskal and Tanner equation yield steep negative exponential curves for the mobile phase such as oil, and flatter negative exponential curves for the gelator phase, such as wax or glycerides, while oleogels or fat blends lie inbetween. NMR diffusometry measurements gave diffusivity values in the range 1×10^{-11} to 1×10^{-10} m^2 s^{-1} across all three studies.

3.11. Magnetic resonance imaging

While NMR gives measurements as spectra and discrete data, the application and detection of RF frequency in multiple axes enables magnetic resonance imaging (MRI) or tomography (Fig. 3k). Just as in ^{1}H NMR, MRI relies on relative proton densities and spin-spin (T_2) relaxation times to generate contrasts between components in mixtures. In particulate food formulations such as chocolate, dry components have low proton densities due to lack of water and can thus be differentiated from organic phases rich in hydrogen-containing hydrocarbons. In the lipid phase, liquid oil can be discerned from solid fat given that the larger triacylglyceride molecules generally have T_2 relaxations of 9–17 ms, while the shorter fatty acids have timescales around 6 ms [10]. MRI was used in several particulate food systems to evaluate oil migration such as palm and peanut oil migration through cocoa butter [89], hazelnut oil filling in contact with chocolate [98], or almond cream layers in contact with dark chocolate [99,100]. While NMR was primarily used on soft matter samples, MRI is suitable for particulate matter inclusions due to the ability to visually discern phases. In contrast, diffusivity is not evaluated directly from detected intensities, but rather from image analysis of reconstructed MRI images. MRI diffusivity values of the mobile oil phase were found to be similar to NMR values across different food systems, between 1×10^{-13} to 8×10^{-10} m^2 s^{-1}. A disadvantage of MRI techniques are the generally the low spatial

resolutions of tens of microns and long acquisition times due the low RF intensity, such that rapid migration phenomena cannot be captured [113].

3.12. X-ray and neutron tomography

Two other prominent tomographic techniques are x-ray computed tomography (XCT) and neutron computed tomography (NCT). While lipid migration techniques employing XCT and NCT are absent, it can provide valuable information on the food microstructure, which in turn aids understanding and model development. Both XCT and NCT are similar in their operation principles (Fig. 3l). X-rays or neutrons are emitted from x-ray or spallation sources aimed at the sample. While x-rays interact with an atom's electrons, neutrons interact with the nucleus. XCT is therefore useful to image hard particulate matter from heavier atoms. Conversely neutrons are more sensitive to atoms with less electrons, such as hydrogen, which makes it more useful for soft fluidic food samples rich in oils and water [113]. To achieve similar imaging contrasts with XCT, contrast agents can be added such as water-soluble potassium iodide for watery phases, or oil-soluble 1,4-diodobenzene for lipid phases. The recorded attenuation of the x-rays or neutron rays are reconstructed in 2D slices that can be rendered in 3D volumes for visual representation of the microstructure. Frequently, further quantification for parameters such as porosity, density, particle size, shape, and surface area is undertaken. Depending on the sample field of view (usually between 0.5 and 5 cm), voxel resolution is in the range of a few 100 nm to a few microns.

XCT has been employed in various food microstructure studies. Reinke et al. [58] simulated stress distributions in chocolate after different tempering conditions by feeding tomogram images to a finite element analysis. Haedelt et al. [114] used XCT to image chocolate with bubble inclusions produced by different foaming gases, leveraging tomographic analysis to correlate bubble size and number with sensory properties. Application and advanced analysis of XCT for edible oil foams (oleofoams) has been extensively covered by Metilli et al. [101]. Neutron tomography on the other hand has been less reported in the literature. Vego et al. [102] harnessed the strength of both XCT and NCT by simultaneous tomographic measurements on a physical two component mixture: couscous particles exposed to humid air. XCT was used to image the solid particulate phase, while NCT was better suited to monitor the hydrogen-rich vapour phase and absorbed water in the food. Spatial and temporal water uptake by the hygroscopic food was thus enabled. The sensitivity of NCT towards water makes it also suitable to analyse drying phenomena. Defraye et al. [115] employed 2D NCT studying the effect of natural and forced convective and radiative drying of apple slices, in presence and absence of the apple peel. Beyond water transport, NCT characterisation of semi-solid starch and spirulina extrudates [103] has been reported. The relatively long exposure times necessary of up to several hours for a single scan make x-ray and neutron ray tomography rather useful for imaging static samples, and less so for dynamic transport phenomena like lipid migration. Synchrotron facilities offer higher performance XCT and NCT infrastructure and may enable future work on more dynamic food systems.

Table 2
Mathematical modelling approaches for oil migration in particulate food systems.

Food system	Model	Fit	Ref
Diffusion			
Cream filling (peanut oil, interesterified hydrogenated palm oil, lecithin, sugar), cocoa butter	$\frac{M_t}{M_\infty} = 4\left(\frac{Dt}{\pi l^2}\right)^{\frac{1}{2}}$	LSE 0 to 0.02	[91]
Fat blend (cocoa butter, tricaprylin, flaxseed oil, safflower oil, peanut oil)	$\frac{M_t}{M_\infty} = \frac{\sqrt{Dt}}{l}$	R^2 0.71 to 0.96	[78]
Fat blend (fully hydrogenated soybean oil, soybean oil, emulsifiers)	$\frac{M_t}{M_\infty} = \frac{\sqrt{D_{eff}t}}{l}$	R^2 0.5 to 0.97	[67]
Fat blend (palm oil+peanut oil layer on cocoa butter with different TAGs)	$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2q+1)^2\pi^2} e^{-\left(\frac{D_{eff}(2q+1)^2\pi^2}{l^2}\right)}$	R^2 0.5 to 0.99	[89]
Fat blend of palm kernel fat and soybean fat with triolein, prefer to use diffusion	$D_{eff} = \frac{0.88w^2}{4t_{1/2}}$	SD 0 to 10%	[90]
Chocolate layer (cocoa liquor, cocoa butter, icing sugar,stevia, sucralose, maltodextrin) in contact with hazelnut paste	$\frac{C(x,t)}{C_\infty} = 1 - e^{kt}\frac{cosx\left(\frac{k}{D}\right)^{\frac{1}{2}}}{cosl\left(\frac{k}{D}\right)^{\frac{1}{2}}} - \frac{16kl^2}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n e^{\left(-\frac{D(2n+1)^2\pi^2 t}{4l^2}\right)}}{(2n+1)\left(4kl^2 - D\pi^2(2n+1)^2\right)} cos\frac{(2n+1)\pi x}{2l}$	R^2 0.81 to 0.91	[98]
Chocolate layer (cocoa liquor, cocoa butter, icing sugar,stevia, sucralose, maltodextrin) in contact with hazelnut paste	$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$ $\text{IC}: C(l,t) = \frac{C_\infty}{1+e^{-k(t-t_0)}}$ $\text{BC}: \frac{\partial C}{\partial x}\Big\vert(x=0) = 0$ $\text{BC}: C(l,t) = C_\infty\vert 1 - e^{-kt}\vert$	R^2 0.91 to 0.99	[98]
Cocoa butter from different geographical locations, tempered vs non-tempered, solubilisation, recrystallisation, diffusion	$M_t = C\left(e^{-k_c t^\beta} - e^{-k_s t^\beta}\right) + k_m\sqrt{t}$	R^2 0.33 to 0.96	[42]
Capillary			
Sunflower oil penetration with emulsifiers into chocolate crumb beds	$L^2 = t\left(\frac{r_{eff}\sigma cos\theta + \Delta P}{2\tau^2\mu}\right)$	R^2 0.99	[116]
Empirical			
Oleogel (rapeseed oil, Myverol, sunflower oil, candelila wax) migrating into contacting paper substrate	$A_{stain} = kt^b$	$R^2 = 0.99$	[77]
Cream filling (peanut oil, interesterified hydrogenated palm oil, lecithin, sugar), cocoa butter; Fat blend (palm oil+peanut oil layer on cocoa butter with different TAGs)	$\frac{M_t}{M_\infty} = \left(1 - e^{-kt}\right)$	$R^2 = 0.98$ to 0.99; SSE = 0.06 to 0.39	[89,91]

4. Modelling of oil migration in particulate food systems

There have been many attempts to model and predict lipid migration in particulate foods as a result of lipid metastability. Depending on the adverse result intended to monitor, such as fat bloom, oil staining on packaging, or the fundamental mass transfer phenomena, different models have been employed. As Tabulated in Table 2, literature can generally be divided into first-principle diffusion and capillary methods, and additional empirical methods that do not emerge from fundamental physical laws.

4.1. Diffusion models

By far the most extensively used models are based on Fick's second law of diffusion. This is mostly due to the mathematical simplicity of basic equations yielding acceptably accurate correlations with experimental results, but also due to the few required input data, compared to capillary models. Diffusion-based models are applicable to fundamental molecular diffusion problems, such as oil migration through a fat matrix, but also allow macroscopic modelling of transport phenomena when the food microstructure is too complex. Particulate systems are complicated and the microscopic flow between multiphasic formulations is generally not purely diffusional transport, especially not in the presence of capillaries. Yet, lumping the effect of different physical phenomena together into a single term and measuring overall properties, an effective diffusivity D_{eff} can be evaluated to feed into diffusion models. Exact D_{eff} measurements depend on the definition of the modeller and the subject microstructure, but for particulate food formulations is generally expressed as

$$D_{eff} = D\frac{\epsilon}{\tau} \tag{15}$$

where ϵ is the void fraction of the structure and τ the tortuosity of the diffusion path. τ is subject to various definitions but is generally the length of the tortuous flow path divided by the straight line connecting its ends [117]. Thus, for a straight path $\tau = 1$, for a semi-circular flow path $\tau = \pi/2$, and for a circle $\tau = \infty$.

Ziegleder [118–120] was the first to comprehensively report the use of Fick's law to model oil migration in chocolate, on which many works have been based to this date, listed in Table 2. Using the simplest form $M_t/M_\infty = (D_{eff}\, t)^{0.5}/l$ the only parameters required to evaluate the diffusivity are thus a measure of oil concentration after a few intervals of time t, for example the concentration, spectral intensity, or mass M_t, the mass or equivalent measure of oil after equilibrium or saturation has been reached M_∞, and the superficial path length l of diffusive transport. It should be noted that here D_{eff} is used and the superficial path length or height of food item – the real diffusivity might be well lower and much more difficult to evaluate, while the real path length might be longer if accounting for void fractions and tortuosity. The attractiveness of diffusion models to bulk food system was used to model peanut oil and palm oil migration through cocoa butter with different lecithin emulsifier ratios and sugar powder by magnetic resonance imaging [91]. The diffusion equation proposed by Peppas and Brannon-Peppas [121] was used, with least squares errors between 0 and 0.02, and yielding diffusivities between 2×10^{-14} to 4×10^{-13} $m^2\ s^{-1}$.

Ziegleder's model was similarly used to model coloured soybean, flaxseed, safflower and peanut oil diffusion through cocoa butter fat blends measured by tracing the coloured oil front with a flatbed scanner [78] and to model soybean oil migration out of a fat matrix into filter paper [67]. The models fitted with correlation coefficients R^2 of 0.5 to 0.96, generally showing the applicability of the diffusion equation in this mostly oil-fat biphasic scenario, yielding diffusivities from 1×10^{-14} to 4.5×10^{-11} $m^2\ s^{-1}$. A more elaborate model to Ziegleder's was used to evaluate diffusivities of palm and peanut oil through cocoa butter with different TAG blends via magnetic resonance imaging, also listed in Table 2 [89]. R^2 statistics of 0.5 to 0.99 were reported with diffusivities of 5×10^{-14} to 6×10^{-13} $m^2\ s^{-1}$, similar to previous work for oil/fat systems, showing again the applicability of Fick's law. In a different work, a diffusion model adapted to the output of the analytical technique was used to evaluate the diffusivities from FRAP measurements [90]. While no fitting statistics of the model were reported, diffusivities of the range 2×10^{-13} to 4×10^{-12} $m^2\ s^{-1}$ were found, similar to findings employing different acquisition techniques. Cikrikci and Oztop [98] used an advanced analytical solution to Fick's second law derived by Crank [122] to model oil migration from hazelnut paste in contact with chocolate via MRI. Diffusivities of 7×10^{-11} to 2×10^{-10} $m^2\ s^{-1}$ and R^2 of up to 0.9 were reported.

A commonality of most previous diffusion models was the discrepancy between model and experimental data especially at early timescales, resulting in poor fits of around $R^2 = 0.5$. Cikrikci and Oztop [98] addressed this issue by using an empirically found logistics model as boundary condition in the diffusion model. The numerically solved solution fitted each experimental data set well with $R^2 > 0.95$ in all cases over the entire timescale.

Besides Fickian diffusion, other models were developed. For example, a solubilisation-recrystallisation-diffusion model was proposed by Marangoni for the migration of the liquid fraction of fats through the solid fat matrix, finding a rate constant for both the solubilisation and recrystallisation. While no formal diffusivity was used, a migration rate constant k_m was incorporated ranging from 0.2 to 1.2 kg $s^{-0.5}$, resulting in R^2 goodness-of-fit values between 0.33 and 0.96.

4.2. Capillary models

By the higher amount of published work it is apparent that diffusion models are popular for modelling oil flow through the fat phase in particulate systems, yet frequently fail to capture fast liquid transport characteristic of capillary flow. While diffusion seems suitable for capturing the rather slow migration processes in chocolate systems, multiple works suggest that oil migration may also involve capillary flow [8]. This has been supported by fast migration measurements in early timescales via EDX that defies the typically longer time scales of diffusion [52]. A recent review highlighted the fallacy of simplifying food transport models to diffusion, showing evidence that many food manufacturing processes such as deep fat frying are more fundamentally explained by capillary action [123]. Many works on liquid imbibition flowing into particulate food structures, as in reconstitution, use capillary models [124]. However in lipid migration studies in which liquid is leaking out of particle structures, capillary models are underrepresented.

Within the area of oil migration under storage conditions, as listed in Table 2, Carbonell [116] used the classical Washburn eq. 8 to model sunflower oil penetration into D_{50} 14–20 μm chocolate crumbs, varying surface tension and viscosity of the penetrating oil. Despite angular nonspherical crumbs it was found that White's equation for effective pore radius r_{eff} yielded predicted void space, while ϵ of the bed was found by nitrogen gas adsorption. R^2 values of 0.99 showed applicability of Washburn's theory to this scenario.

Clearly, research on lipid migration investigating capillary flow is underrepresented. Powerful measurement techniques described earlier such as x-ray tomography now offer means to use more microstructural data and encourages a more granular analysis of lipid migration phenomena.

4.3. Empirical models

The complexity of oil migration processes in particulate foods has also led to the employment of empirical equations not based on fundamental physical understanding but statistical data regression. For rapeseed oil migrating out of a wax oleogel into paper, an exponential n-

th order equation was fitted that modelled the area of expanding oil stain on the packaging substrate, matching with an R^2 of 0.99 [77]. Interestingly, similar to the diffusion and capillary flow models that have an exponent of ½, the exponent here was 0.5 ± 0.001. This suggests oil flow through the oleogel matrix could be modelled as diffusive flow in analogy to the fat cases earlier [67,78,91], while the expanding oil stain on paper could be modelled as capillary flow through a porous medium. Indeed, many authors describe imbibition of liquid into paper via capillary flow approaches, as summarised in this review [22]. Two further works concerned with peanut and palm kernel oil migration through a system of cocoa butter and sugar particles employ an exponential model with goodness-of-fit of $R^2 > 0.98$ [89,91]. While empirical models for oil migration are useful for complex systems that can not readily be analysed with first principle methods, findings are less transferable between food systems and offer less understanding on migration processes and possible mitigation strategies.

Overall, it is evident that diffusion models have attracted the most attention in modelling oil migration, yielding for chocolate systems generally similar diffusivity results across different studies. Capillary models are seldom employed, which is attribute to the additional microstructural data required [123].

5. Mitigation of oil migration in particulate food systems

The adverse sensorial, textural, and technical effects of oil migration have led to an increasing interest in strategies to control and prevent it. Mitigation of oil migration has been approached from multiple directions, such as stabilisation of the oil within the food, such as via oleogelation, pickering emulsification, particle size reduction and capillary suspensions, or encapsulation; enclosing the entire food in an edible coating; or by protecting fibrous packaging to avoid oil staining, illustrated in Fig. 4 and comprehensively summarised in Table 3. Each strategy bears its own advantages and disadvantages, and depending on the approach and final goal, different measurement (and modelling) methods were applied, revealing different success rates in controlling oil migration. With increasing consumers seeking healthy natural diets and moving away from saturated fat intake [28], conventional chemical approaches to oil stabilisation such as esterification and hydrogenation have been omitted, discussing only modern techniques of physical oil stabilisation without chemical modifications.

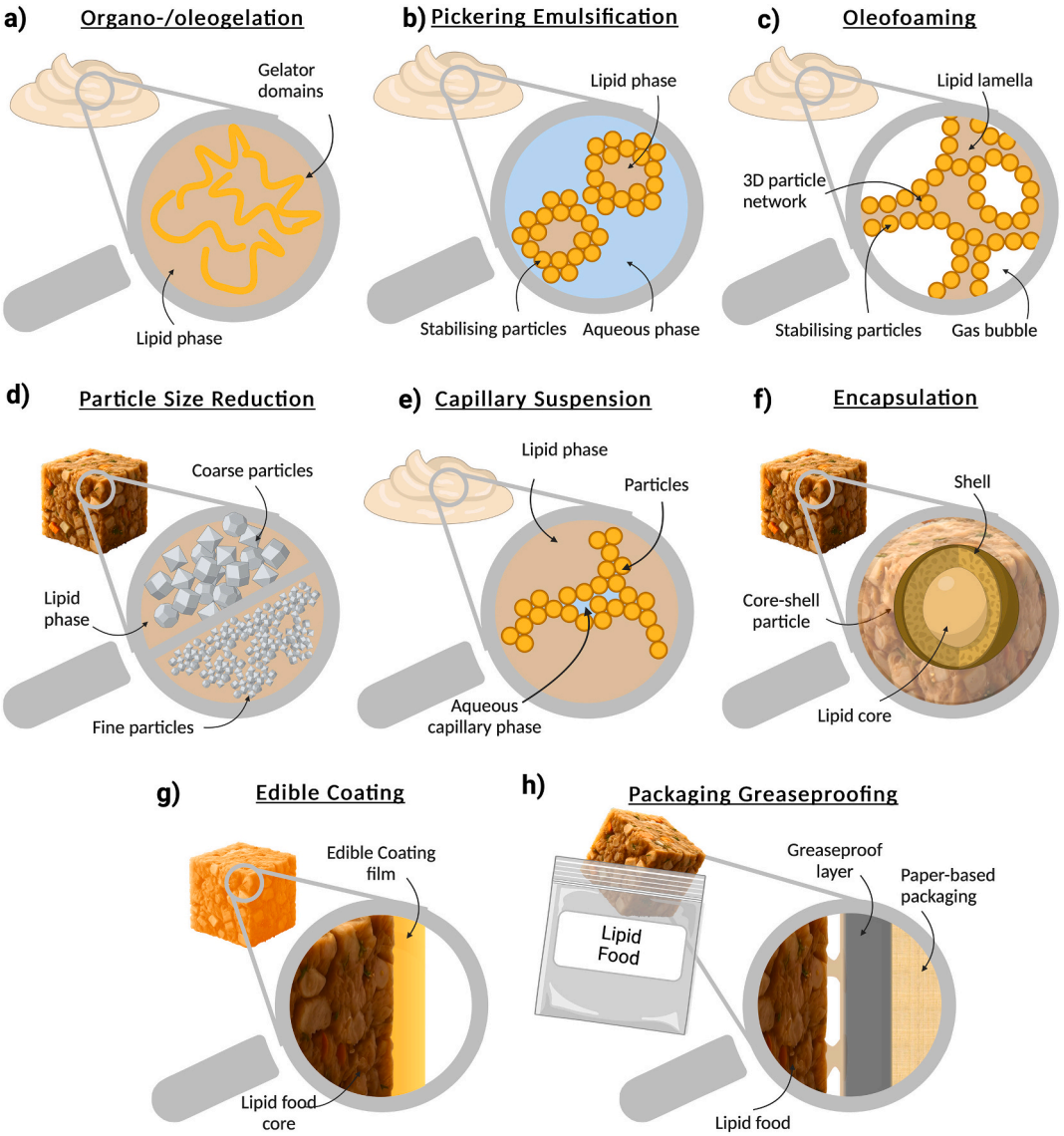

Fig. 4. Strategies for mitigation of oil migration: a) organogelation or oleogelation, b) oleofoaming, c) pickering emulsification, d) particle size reduction, e) capillary suspension, f) encapsulation, g) edible coating, h) packaging grease proofness.

Table 3
Modern oil migration mitigation strategies.

Method	Description	Amount of oil leakage	Advantages (+), disadvantages (-)	Ref
Organo−/oleogelation	Wax-oleogelation of tahini halva with suflower wax, beeswax, shellac between 1 and 5 *w*/w%	< 7% gravimetrically via absorption onto filter paper	(+) Applicable in melted, molded, extruded and pressed products as preparation is a melting-colling process, crystallisation can be influenced by tempering and shearing; (-) subject to labelling, regulatory landscape unclear for bulk products beyond confectionary coating	[125]
	Chocolate with hybrid hydro-oleogel bigel from grape seed oil, beeswax, sodium alginate dispersion	No reduction in WI compared to control sample		[126]
	Chocolate with *Lycium barbarum* seed oil gelated with beeswax, rice bran wax and lacquer wax	< 1.2% gravimetrically after centrifugation		[127]
	High internal phase Pickering oil/water emulsion of corn oil stabilised by proteins	< 6% gravimetrically after centrifugation		[128]
Pickering emulsion	Chocolate ganache emulsion from chocolate and whipped cream, with cocoa powder particles	< 15% gravimetrically after centrifugation	(+) Particles for pickering stabilisation can be native to recipe; (-) only applicable to emulsified products, melting and pressing damages pickering structure	[129]
	Pickering oil/water emulsion from camellia oil, water, and silica particles	50–90% by ethanol extraction		[130]
	Oleofoam from soybean and high oleic sunflower oil with diacylglycerides	0–100% by visual inspection		[131]
Oleofoaming	Oleofoam from sunflower oil and fatty alcohols and fatty acids	2–8% gravimetrically after centrifugation	(+) Health benefits from replacement of lipids with air, particles for foam stabilisation can be native to recipe; (-) foam cannot be mixed or compacted into other products after formation due to bubble collapse	[132]
	Oleofoam from soybean oil, glycerol monostearate, soy protein isolate, and κ-carrageenan	0–100% volumetrically in measuring cylinder		[133]
	Chocolate with various sucrose particle sizes	~ 10% lower migration rate via *WI* and *SG*	(+) No foreign particle introduction required, high oil retention possible, applicable for molten and pressed products; (-) particle size reduction requires energy intensive milling, particle size reduction can influence bulk physical properties	[81]
Particle size reduction	Chocolate with various sucrose particle sizes	~ 10% lower migration rate via *WI* and *SG*		[134]
	Model seasoning cube from salt particle and sunflower oil	0–50% via gravimetry, optical scanning, and Raman spectroscopy		[37]
	Oleogel from zein particles dispersed in soybean oil with water capillary bridges	0% by visual inspection of inverted tests		[135]
Capillary gels/suspensions	Oleogel from wheat middlings dispersed in sunflower oil, with water capillary bridges	9% based on maximum maximum oil holding capacity of pure wheat middlings, gravimetry	(+) No foreign ingredients necessary, only water by capillary bridges required; (-) water migration can impact amorphous and crystalline material	[136]
	Oleogel from zein, whey, and soy protein dispersed in corn oil, with sinapine acqueous solution bridges	40–10% by centrifugation and gravimetry		[137]
	Cinnamon and paprika oleoresins encapsulated in hard palm fat via spray chilling and from saturated gas solutions	2–30% by dispesing in ethanol and spectrophotometry		[138]
Encapsulation	*R. officinalis*, *L. angustifolia*, and *C. aurantium* volatile oil encapsulated in β-cyclodextrin	10–45% by dispersing in ethanol followed by hexane extraction	(+) Potential for controlled release of essential oils; (-) energy-intensive spray drying or other encapsulation processes	[139]
	Chia seed oil with vitamin D3 encapsulated in soy protein isolate, maltodextrin, inulin via spray drying	0–15% by cold hexane extraction		[140]
	Oilve oil in pouches from chitosan, gelatin, and allic acid films	0% by visual inspection of pouches		[141]
Edible coating	Pectin and starch films with eggshell waste particles, in contact with oil (no type specified)	Poor, only qualitative data available	(+) Potential for additional moisture and oxygen barrier included in edible coating; (-) frequently introduces foreign ingredient as coating agent; influences visual appearance	[142]
	Film from sunflower oil cake, sodium alginate and glycerol in contact with sunflower oil	18–34 mg mm m^{-2} d^{-1}		[143]
	Sodium carboxymethyl cellulose and cellulose nanofibrils coated molded pulp trays for fruits packaging	Kit test 12		[144]
Packaging strategies	Alkyl ketene dimer modified sodium alginate coated 60 gsm paper	Kit test 6	(+) Food product unaffected; (-) often difficulties of label printing and appealing visual appearance on shelf with porous material	[145]
	Chitosan and sodium carboxymethyl cellulose coated pizza cardboard box and molded pulp tray	Kit test 12		[146]

5.1. Organo−/oleogelation

Organogelation or oleogelation is an attractive strategy to stabilise the lipid phase in particulate food products, combining high volume fractions of up to >90 *w*/w% liquid oil with small volume fractions down to <10 w/w% of a gelator via melting and cooling, trapping the oil domain in the gelator matrix [147] (Fig. 4a). Rheological studies have shown that even at small gelator loads, the olegeol adapts viscosities higher than the pure oil, thus creating hindrance to oil diffusion. The crystal structure of the gelator can also be influenced by the cooling rate, applied shear during cooling, and ultrasound, influencing the crystal packing density [148,149]. Due to the melting and cooling process in oleogel preparation, this strategy is attractive for molten, molded, tableted or extruded foods, compared to emulsion techniques, offering great potential for oil migration control and saturated fat reduction. Yet, many gelator materials such as waxes require declaration on the ingredient list and as such are scrutinised from a regulatory perspective, hampering wide-spread commercial adoption [30]. In its latest research

applications to chocolate, oleogels prepared from grape seed oil and lyceum barbarym oil, gelated with beeswax, rice bran wax, and lacquer wax, achieved oil retention of up to 98.8 *w*/w% (i.e. 1.2 w/w% oil released from oleogel). Despite reduced oil migration, a decrease in the whiteness index due to fat bloom on chocolate was not measured, suggesting yet more effective oil retention is required [126,127]. In Tahini halva, sunflower oil was oleogelated with beeswax and shellac, reducing oil release to a maximum 7 *w*/w% [125].

5.2. Pickering emulsification

Oil stabilisation from melts is not suitable for heat sensitive foods, for which other strategies are necessary. Pickering emulsification involves small solid particles in dosages as low as 1 w/w% to stabilise the oil-water interface, creating a particle shell around oil or water droplets at the interface [150,151] (Fig. 4b). While elevated temperature or pressure damage the interfacial microstructure, the added particles can be ingredients native to the recipe, or alternatively foreign particles like fat powder [152], amphiphilic particles such as proteins [153], or even janus particles tailored to the lipid and aqueous phases [154] or enhanced interfacial stability. Recently. high internal phase corn oil in water was emulsified by albumin protein, and an oil leakage of <6 w/w % was reported [128]. For chocolate, water-containing whipped cream was stabilised with cocoa particles, resulting in oil leakage of maximum 15 w/w%, exemplifying use of a native material for Pickering stability to reduce oil migration [129]. Involving foreign added particles, camellia oil was stabilised with silica particles, yet oil leakage was higher than in previous works with 50–90 w/w% oil leakage [130].

5.3. Oleofoaming

When the aqueous phase in pickering emulsion is inverted and replaced with air, an oil foam or oleofoam is formed (Fig. 4c). Generally, oleofoams are prepared from oleogels by whipping or sparging with gas. Bubble entrapment then occurs by cooling and solidification in the case of solid fats, by addition of surfactants in the case of liquid oils, or by particle inclusion. Particles can be prepared ex-situ and added to the oleogel, such as proteins or polysaccharides [133], or crystallise from the oleogel in-situ upon cooling, such as for diacyglycerides [131] (Table 3). Stabilisation of the gas-oil interface then occurs by particle adsorption at the interface, reducing the surface energy of the bare particles and bubbles by clustering. Partial oil and gas wettability is thus important to prevent immersion of the particles in either pure phase. Further, interparticle van der Waals and intermolecular hydrogen bonds form a 3D network, stabilising the entrapped bubbles. Destruction of the foam occurs either due to liquid oil drainage out of the lamella, due to dissolution of the gas in the liquid, or due to bubble Oswald ripening [155]. Measurement of this instability is usually quantified as the amount of oil drained by storage under gravity or centrifugation. For microstructural bubble analysis, tomographic techniques have proven useful [101]. Oleofoams have gained importance as a means to partially replace lipids with air, yet adoption outside of niche confectionary or dairy products is limited. The risk of foam collapse makes it less suitable for mixed or compacted products. A study by Ribourg-Birault also found that lipids in oleofoams tend to oxidise faster than in oleogels due to more exposure to oxygen in the bubbles [156]. This issue could be circumvented by air replacement with inert gases such as N_2, CO_2, or N_2O. Oil retention within oleofoams has been reported ranging from 0 to 100% depending on formulation and environmental conditions [155].

5.4. Particle size reduction

Another particle-based strategy in oil migration control is particle size reduction (Fig. 4d). By lowering the particle size but retaining the same mass, surface area of the particles increases while reducing the interparticle distance, thus creating narrower flow channels for the oil and thereby increasing the pressure drop of the oil flow [157–160]. If not advective flow but mass transport via diffusion is expected, particle size reduction creates a more tortuous path, increasing the tortuosity parameter in eq. 15 [161], leading to a reduction in diffusivity. In addition to the dynamic effects of reduced oil flow velocity (advective migration) or diffusion (diffusive migration), the thermodynamic effect of capillarity can be affected. As the inter particle pore size is reduced with smaller particles, capillary radii reduce, increasing the capillary pressure according to the Young-Laplace Eq. 4, suggesting more oil is retained within the food structure. On the other hand, a net increase of surface area results in an increase in particle surface energy, attracting particles towards each other to reduce surface area, which may destabilise the system if particles are sufficiently mobile [35]. Again, this technique is attractive for manufacturing routes involving melting or tableting, as a delicate food structure prone to thermal or mechanical degradation is absent. Moreover, a rigid final structure is desired over a fluid state, to prevent phase separation into solids and liquids induced by the high surface energy particles. Equal to pickering emulsions, the smaller particles can simply be native to the original recipe and do not need to be foreign. Hence particle size reduction of sugar in chocolate systems was tested and oil migration monitored via the whiteness index and surface gloss. As expected, whiteness index formation rate and surface gloss reduction rate was slower for smaller particles, and faster for large particles, thus suggesting a rate decrease for smaller particles. Interestingly, *WI* and *SG* reached plateau values that were the same across all particle sizes after 7 days, suggesting that no oil was statically retained but that the rate reduction was rather dynamic. Mechanistically, this rather suggests a decrease in diffusivity by creation of a more tortuous path caused by the smaller particles, as opposed to an increase in capillary suction pressure that would have retained more oil as the particle size was reduced. Particle size of salt in model sunflower oil-stock tablets was reduced down to 5 μm, achieving 0 *w*/w% oil release, measured gravimetrically, by scanning, and Raman spectroscopy. Due to the liquid nature of sunflower oil and the absence of a fat phase, as was the case in chocolate, oil retention was attributed to capillary action and liquid holdup rather than diffusion [37].

5.5. Capillary suspension

A similar particle-technological approach harnessing capillary action but in a suspended form is termed capillary gels or capillary suspensions involving one solid and three liquid phases. The solid particles are dispersed with tightly controlled ratios of a preferentially wetting liquid and a non-preferentially wetting liquid [162] (Fig. 4e). Depending on the relative ratios of the three phases, ternary mixtures ranging from the pendular state with majoritarily non-preferentially wetting liquid, to the capillary state with majoritarily preferentially wetting liquid are produced. In the latter case, food particles could be native to the recipe avoiding addition of non clean-label components, and the major liquid phase could be oil, while minor amounts of water, < 0.5%, have been reported sufficient to induce capillary stability. Being a soft matter strategy, this technique is less suitable for products undergoing thermal manufacturing due to microstructure collapse. Moreover, the effect of water migration into neighbouring crystalline and amorphous particles needs assessing with regard to crystalline bridge formation or amorphous sintering. Previous reports employed zein or wheat middling particles, suspended in soybean, sunflower, or corn oil stabilised by water or other aqueous solutions. Oil migration measured gravimetrically or by centrifugation ranged from poor 40 to excellent 0 *w*/w% percent [135–137].

5.6. Encapsulation

A complete enclosure of the lipid phase and thus oil migration mitigation is attempted by encapsulation, consisting of the lipid core and a wall substance (Fig. 4f). Various wall materials from $CaCl_2$-crosslinked

sodium alginate to solid fats, sugars, and proteins have been reported [163]. While wall properties can be tuned for controlled release of essential oils for instance, generally the produced capsules are unsuitable for compaction or extensive further processing due to the risk of breakage of the shell. Thus, encapsulated lipids are rather suitable in free-flowing bulk particulate form. Report of cinnamon and paprika oleoresin encapsulated in solid fat via spray drying and saturated gas solution achieved 2–30 w/w/% of oil leakage [138]. For essential oils *R. officinalis*, *L. angustifolia*, and *C. aurantium* encapsulated in β-cyclodextrin, oil migration was reported between 10 and 45 w/w%, while for chia seed oil enclosed in soy protein, maltodextrin, or inulin, oil migration was measured as 0–15 w/w%, using ethanol and hexane extraction methods [139,140].

5.7. Edible coating

A further development of encapsulation as oil mitigation strategy is to not only coat on a microscopic particle or granule level, but to wrap the entire macroscopic food item in an edible wall material, often biopolymers based on proteins or polysaccharides (Fig. 4g). Edible packaging or wrapping has been the subject of many research works, with the potential for additional moisture and oxygen barriers. In fact, for edible packaging moisture and oxygen barrier properties are more frequently investigated than oil barrier performance [164]. The aqueous solutions are usually applied as a spray, curtain, or dip coating, with the disadvantage of large moisture ingress into the hygroscopic food, damaging the microstructure. Additionally, application of a layer usually results in significant visual changes of the food appearance, potentially affecting consumer acceptance. Recent work on edible coatings and packaging specifically to mitigate oil migration reports the use of chitosan, gelatine, and gallic acid mixes to create oilproof pouches, achieving 0% oil leaking [141]. Other works on packaging for human consumption report pectin and starch films with eggshell waste as oil barrier packaging [142], or sunflower oil cake and alginate to package sunflower oil [143]. Yet generally, very little data is reported of the oil barrier properties of the edible coatings.

5.8. Packaging grease proofing

Mitigation of oil migration by stabilising the oil within the food is beneficial to avoid the adverse textural changes within the food due to oil loss (e.g hardening), sensorial effects on the food (e.g. fat bloom) or to avoid food packaging interactions such as oil staining or ink dissolution into oil (Fig. 4h). Yet, in some instances the packaging wrapper might be the last barrier of defence to oil migration. Pressured by consumers and stricter legislation, more sustainable alternatives to conventional plastic, metallised plastic or paper, or *per*- and polyfluoroalkyl treated paper are required [11]. Most modern particle-technological alternative techniques for use in disposable packaging apply fine cellulose-derived fibres or particles in a dry coating process or biopolymer dispersion in a wet coating process in order to create oil-repulsive barriers on the paper surface [165]. Advantages of packaging modifications are of course that the food product remains unchanged, which is beneficial for consumer fidelity, while paper, board or card bear their own challenges such as reduced water and oxygen barrier properties, printability and marketability, and oftentimes higher cost [11]. Applying particle technology, in a recent work, molded pulp trays for fruit packaging was dry coated with sodium carboxymethyl cellulose and cellulose nanofibrils, achieving the highest kit test barrier value of 12 [144]. The same oil barrier performance was achieved when dry coating pizza cardboard boxes with chitosan and sodium carboxymethyl cellulose [146]. For 60 gsm paper, kit test values of 6 were achieved when wet coating with alkyl keter dimer-modified alginate [145], demonstrating that an oil migration barrier is also achievable on the paper side of particulate food-packaging systems.

6. Final remarks

Particle-based consumer foods comprise the majority of fast moving consumer foods, of which many contain lipids in the form of oils, fats, and greases. Multiple factors influence lipid metastability, resulting in lipid migration within, or out of the food structure. This review revisited the factors inducing lipid migration and the most common transport mechanisms diffusion and capillary flow. The ease of application of diffusion models make it the predominant mechanism investigated. Many works on liquid imbibition flowing into particulate food structures, as in reconstitution, use capillary models. However in lipid migration studies in which liquid is leaking out of particle structures, capillary models are underrepresented. Compared to Fickian diffusion models, Washburn-type capillary flow models necessitate more data on the food microstructure, making them challenging to implement. The most common oil migration monitoring methods were revisited, showing the trend towards advanced spectroscopic and tomographic methods. Many macroscopic techniques such as oil stain analysis on paper are performed manually, leaving scope for more objective and efficient measurements using automated imaging tools. Modern mitigation strategies for oil migration control were discussed, with a focus on physical stabilisation approaches as opposed to unpreferred chemical stabilisation. The use of different strategies for different food types and structures is discussed, emphasising the relevance of oil migration issues beyond chocolate, but also for other confectionary and culinary food products consisting of particle-based systems.

CRediT authorship contribution statement

Luc Dewulf: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization. **Michael K. Hausmann:** Writing – review & editing, Supervision. **Annabel Bozon:** Writing – review & editing, Supervision. **Gerhard Niederreiter:** Writing – review & editing, Supervision, Funding acquisition. **Stefan Palzer:** Writing – review & editing, Funding acquisition. **Agba D. Salman:** Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Luc Dewulf reports financial support was provided by Engineering and Physical Sciences Research Council. Luc Dewulf reports financial support was provided by Nestle Research & Development. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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