

Alma Mater Studiorum Università di Bologna
Archivio istituzionale della ricerca

Thermophysical properties of frozen parsley: A state diagram representation

This is the final peer-reviewed author's accepted manuscript (postprint) of the following publication:

Published Version:

Thermophysical properties of frozen parsley: A state diagram representation / Iaccheri E.; Cevoli C.; Dalla Rosa M.; Fabbri A.. - In: JOURNAL OF FOOD PROCESS ENGINEERING. - ISSN 0145-8876. - STAMPA. - 44:4(2021), pp. e13651.1-e13651.7. [10.1111/jfpe.13651]

Availability:

This version is available at: <https://hdl.handle.net/11585/792052> since: 2022-02-03

Published:

DOI: <http://doi.org/10.1111/jfpe.13651>

Terms of use:

Some rights reserved. The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. For all terms of use and more information see the publisher's website.

This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>).
When citing, please refer to the published version.

(Article begins on next page)

This is the peer reviewed version of the following article:

Eleonora Iaccheri, Chiara Cevoli, Marco Dalla Rosa, Angelo Fabbri

Thermophysical properties of frozen parsley: A state diagram representation

Journal of Food Process Engineering Volume 44, Issue 4, April 2021, Article number e13651

which has been published in final form at <https://doi-org.ezproxy.unibo.it/10.1111/jfpe.13651>

This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Use of Self-Archived Versions. This article may not be enhanced, enriched or otherwise transformed into a derivative work, without express permission from Wiley or by statutory rights under applicable legislation. Copyright notices must not be removed, obscured or modified. The article must be linked to Wiley's version of record on Wiley Online Library and any embedding, framing or otherwise making available the article or pages thereof by third parties from platforms, services and websites other than Wiley Online Library must be prohibited.

1 Thermophysical properties of frozen parsley: a state diagram representation

2

3 Eleonora Iaccheri¹, Chiara Cevoli^{1,2*}, Marco Dalla Rosa^{1,2}, Angelo Fabbri^{1,2}

4 ¹ *Interdepartmental Centre for Agri-Food Industrial Research, Alma Mater Studiorum, University of Bologna, Via Quinto*
5 *Bucci 336, Cesena, Italy*

6 ² *Department of Agricultural and Food Sciences, Alma Mater Studiorum, University of Bologna, Piazza Goidanich 60,*
7 *Cesena, Italy*

8 **corresponding author: chiara.cevoli3@unibo.it*

9

10 Abstract

11 Sorption behaviour and glass transition of frozen parsley were investigated in order to study the
12 physical modifications, represented as state diagram to figure out information about product
13 behaviour for storage, and supply chain handling. Frozen products may be located in the state diagram
14 in all the possible freezing temperatures to understand the structure state and study feasible corrective
15 actions mainly focused on temperature and solid content.

16 Parsley was totally dehydrated and equilibrated at selected relative humidity. Sorption behaviour was
17 evaluated by saturated salt slurry method and sorption isotherm fitting, while solid components in
18 terms of mass fraction were investigated by using Differential Scanning Calorimetry. Brunauer-
19 Emmet-Teller (BET) model well fitted with moisture and water activity data ($R^2=0.995$, p -
20 $level<0.05$). The characteristic ranges of stability, in terms of system mobility and physical
21 modification, are the monolayer values (0.240 water activity; 0.052 kg/kg dry basis) and the critical
22 water activity range (0.424 water activity; 0.078 kg/kg dry basis). Glass transition and melting
23 temperature were used to define parsley state diagram. Different zones figure out a specific physical
24 behaviour: depending on solid content and temperature. Unfrozen water was estimated as monolayer
25 BET value 0.84 kg/kg wet basis and extrapolated from state diagram 0.984 kg/kg wet basis.

26

27 **Practical Applications**

28 **Frozen** high-quality product and energy efficiency can be obtained by a correct temperature
29 management. Thermophysical properties of parsley represented in a state diagram are reported in the
30 typical solute and temperature range of freezing process and storage. These data can relate physical
31 structure and temperature, allowing different possible conditions management.

32

33 **Keywords:** frozen parsley; physical properties; state diagram; food chain management

34

35 **1. Introduction**

36 Parsley is worldwide sold as leafy green herb consumed for its own cooking peculiar flavour, but also
37 widely used as ingredient and drugs (Soysal et al., 2006). Because of its high-water content (78–82%,
38 w/w), parsley is ordinarily processed in order to inhibit microorganism growth and prevent
39 degradation (Doymaz et al., 2006). Minimally processed parsley could stay fresh for a period of 23
40 days (Catunescu et al., 2012), but the long-lasting operation induced by freezing produce a peerless
41 shelf lifetime (Tolba et al., 2008).

42 The characterization of biological food tissues is a complicated task, accounting for inhomogeneous
43 arrangement, distribution of cell sizes and shapes, their state and local solute concentrations
44 (Canatella et al., 2004). **Water content and temperature are the most important parameters for physical
45 properties assessment of biological products. The role of water in the physical stability of
46 multicomponent system is critical, particularly regarding mechanical properties (such as crispness,
47 softness, etc.) and structure characteristics (crystallization, collapse, etc.).** Basically, amorphous, and
48 semi-crystalline polymers, that during their industrial processing undergone a fast cooling from
49 environmental temperatures, end up in a **meta-stable** state (Priestley et al., 2005). These modifications
50 over a storage time can show themselves through physical properties changes, such toughness,
51 strength, density, and specific heat (Miles, 1991). Thermophysical properties of foods are mainly
52 dependent on chemical composition, **time**, and temperature. Considering freezing aspects, enthalpy

53 and specific heat capacity of frozen foods are parameters mainly affected by the latent heat of ice
54 fusion (Miles, 1991). Thus, understanding of water/ice equilibrium and phase transition is the basis
55 to understand physical properties of frozen foods. In summary, the whole interpretation of the food
56 frozen system can be simplified and resumed to a two-phase system liquid and dissolved and
57 undissolved solids, with water and dry matter taken as the main components (Fikiin and Fikiin, 1999).
58 Freezing may be subdivided in several **stages**. The precooling **stage**, in which the material is cooled
59 from an initial temperature to the initial freezing point, that is the highest temperature at which ice
60 may exist in a food in thermal equilibrium (Miles, 1991). It should be considered that not all the water
61 can be converted into ice at this transition temperature (Roos, 2012), **so a phase change period is**
62 **present as crystallization of the majority part of water required time** (Miles, 1991). Finally, a further
63 reduction of temperature is of central importance to freeze water, the so-called tempering stage in
64 which food during time reaches a final established temperature. The quantity of ice increases **as a**
65 **function of decreasing temperature until a plateau, when** this phenomenon goes more slowly. Hence,
66 water and ice rate in every foodstuff is highly time dependent (Miles, 1991). Considering the
67 differences between water and ice physical properties, water phase transitions rule frozen food
68 modifications. Thus, the main physical changes occurring during frozen conditions depending on
69 moisture migration and ice recrystallization (Roos, 2012)

70 An easy way to show these phases, correspondent to different physical properties of a frozen food, is
71 depicting a stability map able to describe relations among water in the amorphous and crystalline
72 phase, solute freeze concentration and the residual unfrozen water, highlighting the critical zones. In
73 this way, different states of a food as a function of soluble solids and temperature of state transition
74 were displayed to build up a state diagram. In literature, food stability has been formerly reported as
75 a function of thermo physical modifications due to a second order thermodynamic transition, such as
76 glass transition, in which the material undergoes a change in **phase** but not in **state** (Roos, 1991)
77 Particularly, the concept of food state diagram based on glass transition and freezing curve has been
78 proposed in the '90s by Roos and Karel, and since then by several other authors (Roos, 1991; Sá and

79 sereno, 1994; Figueiredo et al., 1999; Rantanen et al., 2000; Melton et al., 2002; Rahman, 2004;
80 Rahman, 2006 Rahman, 2009; Guizani et al., 2010; Rahman, 2012; Zhao et al., 2015; Suresh et al.,
81 2017).

82 Frozen products could be located in the state diagram as a function of solids content and temperature.
83 Based on the location in a defined zone it is possible to estimate the stability of the foodstuff and
84 develop strategies for storage design and management. The objective of this work is to explore the
85 concepts of state diagram and glass transition to figure out the thermophysical properties of frozen
86 parsley.

87

88 **2. Material and methods**

89

90 *2.1 Samples preparation*

91 Frozen parsley was purchased in a commercial supermarket in Cesena, Italy. Frozen parsley was
92 chosen to investigate the humidity influence and physical properties of a disintegrated cellular
93 structure, in order to well evaluate the possible behaviour of products under storage and distribution
94 conditions. Three packages were employed, and the ingredients of the final product were parsley and
95 sunflower oil (maximum 3%, for preservation purposes). Short time after purchasing, the products
96 was de-frozen at environmental temperature, $22^{\circ}\text{C} \pm 1$, then water content and glass transition for de-
97 frozen parsley was stated at 4.57 kg/kg dry basis and -48.64°C , respectively.

98 All the samples were then conditioned for about 30 days into a desiccator containing phosphorus
99 pentoxide (P_2O_5) in order to dehydrate and stabilize the samples to the minimum water activity, about
100 0. Hereafter samples were rehydrated as reported in the following subsection.

101

102 *2.2 Sorption isotherm*

103 Traditional saturated salt slurry method (DES) was carried out for sorption isotherms assessment.
104 DES method consists in the achievement of a defined hydration level of samples, imposed by salt

105 solution saturation. The salt solution produces a relative humidity of the closed environment, and
106 time is required to the samples to reach a thermodynamic equilibrium with the surrounding
107 atmosphere. Dehydrated parsley samples were positioned inside a hermetically closed desiccator
108 containing, on the bottom, different saturated salt solutions (LiCl, $\text{KC}_2\text{H}_3\text{O}_2$, MgCl_2 , K_2CO_3 , NaBr,
109 and NaCl). The thermodynamic equilibrium was evaluated by weighting samples three consecutive
110 times, considering a steadiness at $\Delta_{\text{weight}} < 0.0005$.

111 Water activity of the equilibrated samples was measured by a dewpoint hygrometer, mod. Aqualab
112 (Decagon Devices Inc., Pullman, WA). Moisture was evaluated by oven method (AOAC 934.06, dry
113 oven at 70°C until steady weight) and hereafter expressed as water content on dry basis for moisture
114 sorption isotherms and as solid content on wet basis for state diagram representation. All the analyses
115 were conducted at least in triplicates. BET equation was chosen to fit experimental data of water
116 content and water activity:

$$118 \quad X = \frac{V_m C a_w}{(1-a_w)(1+(C-1)a_w)} \quad (1)$$

119
120 X is the water content (kg/kg dry basis), V_m is the water content of the monolayer (kg/kg dry basis)
121 and C is the constant related to monolayer sorption heat. According to the literature, BET equation is
122 the best ways to determine the sorption behaviour in mid-low water activity range, particularly it well
123 estimates monolayer moisture content, fundamental parameter for product stability defining the
124 quantity of water un-available for physical structure modifications (Ross, 1991).

126 2.3 Differential Scanning Calorimetry

127 The glass transition temperature (T_g) and the initial freezing point were evaluated in triplicate by
128 using a DSC mod. Q20 (TA Instrument, Germany). The DSC was connected to a low-temperature
129 cooling unit mod. System90 (TA Instrument, Germany). For calibration, the same heating rate used

130 for sample measurement was applied under a dry nitrogen gas flux of 50 mL/min. Heat flow was
131 calibrated using the heat of fusion of indium (ΔH 28.71 J/g). Each sample (about 1 mg) was weighed
132 in 50 μ l hermetic aluminium pans and then loaded into the DSC instrument at room temperature,
133 using an empty pan for reference. Samples were equilibrated at -35°C for 10 min, and then two heat-
134 cool cycles were applied from -90 to 80°C at 5°C/min. Variations of heat flux (V), displayed as
135 thermogram base line deviations in terms of peak and step changes of the baseline, were evaluated
136 by using the automatic tool of the Software TA-Universal analyser (TA Instrument, Germany).

137

138 *2.4 Glass transition fitting*

139 The Gordon and Taylor model (eq. 2) was applied to experimental data:

140

$$141 \quad T_g = \frac{T_{g_s} X_s + k T_{g_w} X_w}{X_s + k X_w} \quad (2)$$

142

143 T_g , T_{g_s} and T_{g_w} are the glass transition temperatures of the sample, solid and water, respectively,
144 instead X_s and X_w are the percentage of solid and water content in the sample, and k is the calculated
145 parameter. The T_{g_w} was taken as -135°C, according to average value of the literature data (Roos,
146 1995). Gordon and Taylor equation describes the composition dependence of the transition
147 temperature of amorphous components, and it is usually used for T_g prediction (Gordon and Taylor,
148 1952).

149

150 **3.Results and discussion**

151 *The influence of water on molecular mobility is pronounced on system where moisture content is*
152 *restricted, such as frozen parsley.* Prediction of the physical state was based on water mobility
153 *assessment in temperature and humidity domains, and* also on modelling water plasticization, thus T_g

154 depression with increasing water content. Sorption data and T_g determination allow the description
155 of changes in physical state that may occur during processing and storage conditions.

156 Thermal properties of parsley were obtained by using DSC. The annealing conditions selected,
157 holding samples at -35°C , allowed the maximum ice formation leading to a maximum solid part
158 concentration since water solidified alone creating a soluble solid amorphous concentrated phase.
159 Two examples of parsley thermograms are shown in figure 1.

160 Thermogram of sample equilibrated at 69% of relative humidity (RH) (Fig. 1a) showed ice formation
161 on freezing and rewarming. Ice formation is a first order state transition of water, the passage from
162 liquid to solid and vice versa, it is detected by maximum value of peak correspondent to melting
163 temperature (T_m) and crystallization temperature (T_c). Sample equilibrated at 17% of RH (Fig. 1b)
164 reported no ice formation. Ice melting was found for samples equilibrated at RH higher than 24%.

165 No ice formation means unfrozen water presence, water unavailable to solidified alone. Un-freezable
166 water is the amount of water remaining unfrozen as un-crystallized free water or bound to the solid
167 matrix even at low temperature (Raman et al. 2006). Different state of water could be measured in
168 several way, such as sorption isotherms with monolayer, multilayer concepts or unfreezeable water
169 estimated by DSC (Raman et al. 2006). Several authors estimated un-freezable water content
170 comparing DSC endotherms of samples having freezable water from the plot of melting enthalpy
171 (Roos, 1991). This procedure was used for crackers (Given, 1991), strawberry (Roos, 1987), dates
172 (Rahman, 2004), sucrose (Ablett et al., 1992), cabbage (Paakkonen & Plit 1991) and garlic (Rahman
173 et al., 2005a).

174 In table 1 the averaged value of temperature for both glass transition and melting point of water in
175 parsley at each a_w levels are reported.

176 T_g ranges from -5.02 to -46.71°C and, as expected, T_g decrease with water content increase. Melting
177 point at $0.172 a_w$ was not detected, due to water unavailability according to literature (Duckworth &
178 Smith, 1963).

179 Linear relation between T_g and a_w can be calculated in addition to sorption isotherm to build a stability
180 map useful for predicting T_g of materials stored at various conditions (figure 2).

181 The sorption isotherm of parsley at 22°C was fitted with BET model with a good determination
182 coefficient ($R^2=0.995$, $RMSE=0.02$, $p\text{-level}<0.05$) confirming that the model well described the low
183 moisture region of sorption profiles. The calculated monolayer value X_m corresponded to an a_w of
184 0.24 and a water content of 0.052 kg/kg dry basis. BET monolayer was previously reported as un-
185 freezable water and contributed to metastability of frozen product evaluation (Labuza et al., 1972;
186 Rahman, 2009; Ross, 2012). The monolayer value is the limit under which water is strictly bound to
187 the matrix, hence represent the most stable zone in terms of moisture mobility.

188 The linear relation created by using experimental data of T_g and a_w was used to calculate the critical
189 a_w value. This critical value was calculated by using the used storage temperature of frozen product
190 (-26°C) and correspond to a water activity of 0.424. According to sorption isotherm the corresponding
191 water content expressed on dry basis is 0.079 kg/kg. Above this critical value physical modifications
192 begin, such as loss of crispness, stickiness of powder and hard candies, recrystallization of amorphous
193 sugars causing caking, mechanical modification including collapse phenomena, loss of porosity as
194 well as diffusion (Gordon and Taylor, 1952; Labuza et al., 1972; Ross, 2012).

195 Actually, this map can give important indications about product stability. Despite this, equilibrium
196 freezing conditions influenced by the amount of ice formed on temperature and composition are
197 missing information. Freezing curve and glass transition data were implemented in a state diagram to
198 draw several regions with different physical states, as previously reported in literature (Raman 2004,
199 Raman et al. 2006).

200 State diagram of parsley is shown in figure 3. The state diagram was built starting from temperature
201 and solid content data. T_{gw} and T_{gs} are glass transition of water and totally dried product, respectively.
202 Glass transition of the product at different solid contents are reported, with grey dot, in between and
203 fitted with Gordon Taylor equation (eq. 2). The Gordon and Taylor model show good coefficient of

204 determination value ($R^2=0.958$, $RMSE=0.17$, $p\text{-level}<0.05$). The value of the calculated k parameter
205 is 3.78, comparable to literature k values of foodstuff (Sá and Sereno, 1994).

206 The melting temperatures of onset and end point were added to figure out different zone of solute,
207 solution, and solid presence. The freezing curve is created from T_{mw}^I and T_m^{end} of the product at the
208 higher hydration level (a_w 0.693). B is the melting temperature at the end freezing point. The
209 intersection of vertical interpolation from B to the T_g curve is the point A. The point A is known as
210 unfrozen water. The extrapolated solid content is 0.84 kg/kg wet basis. Similar solid contents were
211 reported in literature for date flesh and garlic (Rahman, 2006, 2005), even if attention to wet or dry
212 basis should be paid to avoid misinterpretation. The calculated solid content of monolayer X_m of the
213 BET equation, other expression of unfrozen water is 0.948 kg/kg wet basis, as expected in agree with
214 state diagram. BET-monolayer solid content value is used as un-freezable water quantification and it
215 can be determined by using different methods. As several works reported (Rahman 2006, 2009,
216 2012), parsley un-freezable water calculated with BET-monolayer value is higher than that of the
217 extrapolated from the state diagram. These stability values are of utmost importance for process and
218 storage management, as parameters influencing product stability. Several authors (Roos and Karel,
219 1991; Sá and Sereno, 1994), reports the temperature storage dependence on product degradation.
220 Particularly, it suggests a simple index based on $T_{storage}-T_g$. In this way if T_g correspond to storage
221 temperature no degradation occurs. For frozen food stored at about -26°C this corresponds roughly
222 to the moisture content of the critical water activity, well under the typical frozen product. As guess,
223 frozen vegetables are not totally stable, with time dependent chemical-physical modifications.

224

225 **Conclusions**

226 The present study maps the phase modification of liquid, rubbery, glassy, and crystal components of
227 parsley by means of a stability map and a state diagram as a function of water content, solid content,
228 and temperature.

229 The sorption profile of parsley was assessed and integrated with glass transition temperature to draw
230 a stability map. Thermophysical properties of parsley, such as glass transition and melting point, were
231 measured. The temperature ranges from 20 to -135 allowing an easily visualization of the typical
232 process and storage temperatures of freezing. Different zone delineated in the state diagram are
233 characterized by different physical structures of parsley characterized as a function of water and
234 temperature. Considering the supply cold chain of frozen products, the state diagram could provide
235 useful data in terms of critical temperature strictly related to the product physical modification and
236 hence the final quality.

237 Further work should be done to extend the solid content range and implement the state diagram with
238 deliquescent point data, to provide information also referring to the [drying](#) process.

239

240 **Acknowledgements:** This work was supported by CoACh project - Cold management in Agro-food
241 Chains: solutions for process digitalization (Grant number (CUP): CUPD41F18000060009), co-funded
242 by the Emilia-Romagna Region through the POR FESR 2014e2020 funds (European Regional
243 Development Fund).

244

245 **References**

246 Ablett, S., Izzard, M. J., & Lillford, P. J. (1992). Differential scanning calorimetric study of frozen
247 sucrose and glycerol solutions. *Journal of the Chemical Society Faraday Transactions*, 88(6), 789–
248 794.

249 Canatella, P.J., Black, M.M., Bonnichsen, D.M., McKenna, C., Prausnitz, M.R., (2004). Tissue
250 Electroporation: Quantification and Analysis of Heterogeneous Transport in Multicellular
251 Environments. *Biophysical Journal*, 86, 3260–3268. [https://doi.org/10.1016/S0006-3495\(04\)74374-](https://doi.org/10.1016/S0006-3495(04)74374-X)
252 X.

253 Catunescu, G.M., Tofana, M., Crina, M., David, A. (2012). Sensory Evaluation of Minimally
254 Processed Parsley (*Petroselinum crispum*), Dill (*Anethum graveolens*) and Lovage (*Levisticum*

255 officinale) Stored at Refrigeration Temperatures. Bull. Univ. Agric. Sci. Vet. Med. Cluj-Napoca -
256 Agric. 69, 205–212. <https://doi.org/10.15835/buasvmcn-agr:8762>.

257 Doymaz, I., Tugrul, N., Pala, M. (2006). Drying characteristics of dill and parsley leaves. Journal of
258 Food Engineering, 77, 559–565. <https://doi.org/10.1016/j.jfoodeng.2005.06.070>.

259 Duckworth, R. B., & Smith, G. M. (1963). The environment for chemical change in dried and frozen
260 foods. Proceedings of the Nutrition Society, 22, 182–189.

261 Figueiredo, A.M., Sereno, A.M., Sa, M.M. (1999). Glass transitions and state diagrams for fresh and
262 processed apple, Thermochimica Acta, 329, 31–38.

263 Fikiin A.K., Fikiin, G.A. (1999). Predictive equations for thermophysical properties and enthalpy
264 during cooling and freezing of food materials, Journal of Food Engineering, 40, 1–6.
265 [https://doi.org/10.1016/S0260-8774\(99\)00026-6](https://doi.org/10.1016/S0260-8774(99)00026-6).

266 Gordon, M, Taylor, J. S., (1952). Ideal copolymers and the second-order transitions of synthetic
267 rubbers. I. Non-crystalline copolymers, Journal of Applied Chemistry, 2, 493-500.
268 <https://doi.org/10.1002/jctb.5010020901>.

269 Given, P.S., (1991). Molecular behavior of water in a flour–water baked model system. Levine, and
270 L. Slade (Eds.), Water relationships in food, vol 302, 465–483, New York: Plenum Press.

271 Guizani, N., Al-Saidi, G.S., Rahman, M.S., Bornaz, S., Al-Alawi, A.A. (2010). State diagram of
272 dates: Glass transition, freezing curve and maximal-freeze-concentration condition, Journal of Food
273 Engineering, 99, 92–97. <https://doi.org/10.1016/j.jfoodeng.2010.02.003>.

274 Labuza, T.P., McNally, L., Gallagher, D., Hawkes, J., Hurtado, F. (1972). Stability of intermediate
275 moisture foods, Journal of Food Science, 37, 154–159. <https://doi.org/10.1111/j.1365-2621.1972.tb03408.x>.

277 Melton, L.D., Rahman, M.S., Bai, Y., Perera, C.O., Smith, B. (2002). State diagram of apple slices:
278 glass transition and freezing curves, Food Research international, 34, 89–95.
279 [https://doi.org/10.1016/s0963-9969\(00\)00128-9](https://doi.org/10.1016/s0963-9969(00)00128-9).

280 Miles, C.A. (1991). *The Thermophysical Properties of Frozen Foods*. Springer Series in Applied
281 Biology, 45–65. https://doi.org/10.1007/978-1-4471-3446-6_4.

282 Paakkonen, K., & Plit, L. (1991a). Equilibrium water content and the state of water in dehydrated
283 white cabbage. *Journal of Food Science*, 56(6), 1597–1599.

284 Priestley, R.D., Ellison, C.J., Broadbelt, L.J., Torkelson, J.M. (2005). Materials Science: Structural
285 relaxation of polymer glasses at surfaces, interfaces, and in between, *Science*, 80, 456–459.
286 <https://doi.org/10.1126/science.1112217>.

287 Rahman, M.S. (2004). State diagram of date flesh using differential scanning calorimetry (DSC),
288 *International Journal of Food Properties*, 7, 407–428. <https://doi.org/10.1081/JFP-200032930>.

289 Rahman, M.S., Sablani S.S., Al-Hasbi N., Al-Maskri S., Al-Belushi R. (2005). State diagram of
290 freeze-dried garlic powder by differential scanning calorimetry and cooling curve methods. *Journal*
291 *of food science*, 70 (2), E 135-141, <https://doi.org/10.1111/j.1365-2621.2005.tb07086.x>

292 Rahman, M.S. (2006). State diagram of foods: Its potential use in food processing and product
293 stability. *Trends Food Sci. Technol.* 17, 129–141. <https://doi.org/10.1016/j.tifs.2005.09.009>.

294 Rahman, M.S. (2009). Food stability beyond water activity and glass transition: Macro-micro region
295 concept in the state diagram, *International Journal of Food Properties*. 12, 726–740.
296 <https://doi.org/10.1080/10942910802628107>

297 Rahman, M.S. (2012). Applications of macro-micro region concept in the state diagram and critical
298 temperature concepts in determining the food stability, *Food Chemistry*, 132, 1679–1685.
299 <https://doi.org/10.1016/j.foodchem.2011.09.092>

300 Rantanen, J., Räsänen, E., Tenhunen, J., Käsäkoski, M., Mannermaa, J.P., Yliruusi, J. (2000). In-
301 line moisture measurement during granulation with a four-wavelength near infrared sensor: An
302 evaluation of particle size and binder effects, *European Journal of Pharmaceutics and*
303 *Biopharmaceutics*, 50, 271–276. [https://doi.org/10.1016/S0939-6411\(00\)00096-5](https://doi.org/10.1016/S0939-6411(00)00096-5).

304 Roos, Y. H. (1987). Effect of moisture on the thermal behavior of strawberries studied using
305 differential scanning calorimetry. *Journal of Food Science*, 52(1), 146–149.

306 Roos, Y., Karel, M. (1991). Applying state diagrams to food processing and development. Food
307 Technology. PubMed 45 (12): 66, 68-71, 107.

308 Roos, Y.H. (2012). Materials Science of Freezing and Frozen Foods. Food Mater. Wiley Online
309 Library. Sci. Eng. 373–386. <https://doi.org/10.1002/9781118373903.ch14>

310 Sá, M.M., Sereno, A.M. (1994). Glass transitions and state diagrams for typical natural fruits and
311 vegetables, *Thermochimica Acta*, 246, 285–297. [https://doi.org/10.1016/0040-6031\(94\)80096-0](https://doi.org/10.1016/0040-6031(94)80096-0).

312 Guizani, N., Al-Saidi, G.S., Rahman, M.S., Bornaz, S., Al-Alawi, A.A., 2010. State diagram of
313 dates: Glass transition, freezing curve and maximal-freeze-concentration condition. *J. Food*
314 *Eng.* 99, 92–97. <https://doi.org/10.1016/j.jfoodeng.2010.02.003>

315 Melton, L.D., Rahman, M.S., Bai, Y., Perera, C.O., Smith, B., 2002. State diagram of apple slices:
316 glass transition and freezing curves. *Food Res. Int.* 34, 89–95. [https://doi.org/10.1016/s0963-](https://doi.org/10.1016/s0963-9969(00)00128-9)
317 [9969\(00\)00128-9](https://doi.org/10.1016/s0963-9969(00)00128-9)

318 Rahman, M.S., 2012. Applications of macro-micro region concept in the state diagram and critical
319 temperature concepts in determining the food stability. *Food Chem.* 132, 1679–1685.
320 <https://doi.org/10.1016/j.foodchem.2011.09.092>

321 Rahman, M.S., 2006. State diagram of foods: Its potential use in food processing and product
322 stability. *Trends Food Sci. Technol.* 17, 129–141. <https://doi.org/10.1016/j.tifs.2005.09.009>

323 Roos, Y., Karel, M., 1991. Applying state diagrams to food processing and development. *Food*
324 *Technol.* 45.

325 Sá, M.M., Sereno, A.M., 1994. Glass transitions and state diagrams for typical natural fruits and
326 vegetables. *Thermochim. Acta* 246, 285–297. [https://doi.org/10.1016/0040-6031\(94\)80096-0](https://doi.org/10.1016/0040-6031(94)80096-0)

327 Soysal, Y., 2006. Microwave Drying of Parsley : Modelling , Kinetics , and Energy Aspects 93,
328 403–413. <https://doi.org/10.1016/j.biosystemseng.2006.01.017>

329 Suresh, S., Al-Habsi, N., Guizani, N., Rahman, M.S. (2017). Thermal characteristics and state
330 diagram of freeze-dried broccoli: Freezing curve, maximal-freeze-concentration condition, glass line
331 and solids-melting, *Thermochimica Acta*, 655, 129–136. <https://doi.org/10.1016/j.tca.2017.06.015>

332 Tolba, K.H., Youssef, S.M., Abd-Elwahab, E.S. (2008). Physicochemical Properties and Its
333 Application of Dill (*an-Ethum Graveolens*) and Parsley (*Petroselinum Sativum*) and Their Essential
334 Oils, Arab Universities Journal of Agricultural Science, 16, 379–387.
335 <https://doi.org/10.21608/ajs.2008.14953>

336 Zhao, J.H., Liu, F., Wen, X., Xiao, H.W., Ni, Y.Y. (2015). State diagram for freeze-dried mango:
337 Freezing curve, glass transition line and maximal-freeze-concentration condition, Journal of Food
338 engineering, 157, 49–56. <https://doi.org/10.1016/j.jfoodeng.2015.02.016>