Inferring equilibrium and pseudo-equilibrium pVT properties of super-glassy polymers from gas solubility data

Roberto Parchi, Matteo Minelli, Giuseppe Pangia, Ferruccio Doghieri

[a] Department of Civil, Chemical, Environmental and Materials Engineering, University of Bologna, 40126 Bologna,

E-mail: roberto.parchi2@unibo.it

Glassy polymers are widely used in the chemical, pharmaceutical, and biomedical industries. Recently developed materials in this class, characterized by extremely high free volume (super-glassy polymers), promise exceptional performance in key applications such as protective coatings, drug delivery devices, and membranes for gas or liquid separations. This approach presents the ambitious challenge of replacing or integrating thermal separation technologies to reduce CO_2 emissions and energy consumption, or to concentrate CO_2 in carbon capture processes.

For the design of materials aimed at such uses, a reliable and comprehensive representation of the thermodynamic properties of both the pure polymer and the polymer-solute mixture is essential. This remains a challenging task for glassy materials, due to their inherently non-equilibrium nature. One of the most straightforward and effective methods proposed for describing properties in polymer-solute systems below the glass transition temperature is the Non-Equilibrium Thermodynamics of Glassy Polymers (NET-GP). However, its application to predicting gas and vapor solubility requires knowledge of both equilibrium and non-equilibrium volumetric properties of the pure polymer. This represents a significant obstacle for analysing sorption in super-glassy polymers, since equilibrium properties cannot be directly measured, as glass transition temperatures often exceed degradation temperatures, and pseudo-equilibrium properties are sensitive to preparation protocols and aging.

In this work, a recently introduced method called “dual Non-Equilibrium Lattice Fluid” (d-NELF) is used to retrieve equilibrium and pseudo-equilibrium free volume for polymeric species by analysing experimental gas solubility isotherms. The procedure is applied to materials in the class of polymers of intrinsic microporosity (PIMs) and other super-glassy polymers. These results are then used within the NET-GP framework to predict vapor sorption in the same high-free-volume matrices, with predictions compared against experimental data from the literature. In this way, we present a novel comparison between equilibrium and pseudo-equilibrium volumetric properties across different glassy polymers, as well as within the same polymer subjected to various physical treatments. This characterization using the d-NELF approach enhances the accuracy of solubility predictions in these materials by providing more consistent input parameters, thus improving the reliability of thermodynamic modelling in non-equilibrium conditions.

Keywords: *Equation of State (EOS), pVT properties, d-NELF, NET-GP, glassy polymers, gas sorption,*