Phase diagram of length polydisperse Yukawa chain fluid

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An extension of the dimer version of Wertheim's thermodynamic perturbation theory is proposed and used to treat polydisperse mixture of the hard-sphere Yukawa chain fluid with chain length polydispersity. The structure and thermodynamic properties of the reference system, represented by the multi-component mixture of the Yukawa hard-sphere dimers, is described using polymer mean spherical approximation. Explicit analytical expressions for the Helmholtz free energy, chemical potential and pressure in terms of the two chain length distribution function moments are derived. The theory is used to calculate the full liquid-gas phase diagram, including critical binodal, cloud and shadow curves and distribution functions of the coexisting phases. Effects of fractionation in terms of the distribution function and its first and second moments are studied. Theoretical results of the theory at hand and employed recently high temperature approximation are in qualitative agreement with corresponding experimental predictions for the polydisperse mixture of the polymers in a single solvent. In particular both theory and experiment predict that longer chain polymers equilibrate to the liquid phase and shorter chain polymers are predominantly encountered in the gas phase.