

Kumar, Szleifer, and Panagiotopoulos Reply: The main point of the Comment [1] is to show that the incremental chemical potential of a polymer chain is a function of chain length. *This is consistent with the interpretation of this quantity* in our Letter [2]. The incremental chemical potential between a chain of length ν and one of length $\nu+1$ is a well-defined thermodynamic quantity, and no assumptions about its chain length dependence have been made in its derivation [Eq. (10) of our Letter [2]]. To illustrate this point further we present a derivation that re-

lates incremental chemical potentials to the chemical potential of whole chains, which is the quantity utilized by Frenkel and Smit [3]. Consider the definition of the chemical potential of a chain of length ν , $\mu_{\text{chain}}(\nu)$, which is Eq. (4) in our original paper [2],

$$-\beta\mu_{\text{chain}}(\nu) = \ln Z(N, \nu) - \ln Z(N-1, \nu), \quad (1)$$

where β is the thermodynamic temperature, and N is the number of chains in the system. This equation can immediately be rewritten as

$$\exp[-\beta\mu_{\text{chain}}(\nu)] = \frac{Z(N, \nu)}{Z(N-1, \nu, 1, \nu-1)} \frac{Z(N-1, \nu, 1, \nu-1)}{Z(N-1, \nu, 1, \nu-2)} \dots \frac{Z(N-1, \nu, 1, 1)}{Z(N-1, \nu)}, \quad (2)$$

where $Z(N-1, \nu, 1, x)$ corresponds to a partition function where we have $N-1$ chains of length ν , and one chain of length x , where $x < \nu$. Following the procedure proposed in Ref. [2] Eq. (2) simplifies to

$$\mu_{\text{chain}}(\nu) = \mu_r(\nu) + \mu_r(\nu-1) + \dots + \mu_r(1), \quad (3)$$

where $\mu_r(x)$ corresponds to an incremental chemical potential between a chain of length x and one of length $x-1$. The left-hand side, which is the chemical potential of a whole chain, is the quantity obtained by the technique presented by Frenkel and Smit [3] and it is shown to be formally equal to a sum of incremental chemical potentials. Again, no assumption of the chain length dependence of either quantity is made or required, and the information content in either definition of chemical potential is the same.

As noted in the Comment [1] the incremental chemical potential is not constant at zero density and $T^*=2$. While this is an important point, it does not contradict Fig. 2 of our Letter [2] which shows that the incremental chemical potential is indeed weakly chain length dependent for ν larger than ca. 10. In addition, one of us has, in a separate publication [4], shown results for the length dependence of the nonbonded contribution to the incremental chemical potentials that are in *quantitative agreement* with results obtained from the technique discussed in the Comment. It is therefore stressed that all assumptions made in our Letter [2] regarding the chain length dependence of the incremental chemical potentials represent *convenient approximations*, and do not reflect any inadequacy or uncontrolled approximation made in the derivation of this quantity.

In our Letter [2] we have presented an estimate for the liquid-gas coexistence for a relatively short oligomer by assuming that the incremental chemical potential is independent of chain length. The fact that the nonbonded contribution at zero density is weakly chain length dependent is not important in this context since the dominant contribution arises from the ideal gas contribution.

In conclusion, we stress that the technique presented by Frenkel and Smit [3] for the calculation of the chemical

potentials of whole chains is complete equivalent to the modified Widom method presented in our Letter [2]. The incremental chemical potentials determined in this fashion are not necessarily independent of the chain length of the chain molecules in question, as explicitly stated in the original article: "We can thus estimate the chemical potential of a chain of arbitrary length by multiplying the incremental chemical potential by the number of beads in the chain, and adding corrections from simulations of short chains for which the incremental chemical potential is a function of chain length." It will be of general interest, as pointed out in the Comment [1], to determine the chain length beyond which the incremental chemical potentials are independent of chain length, but this point is beyond the scope of this Reply.

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