Adam-Gibbs Relation for Glass-Forming Liquids in Two, Three, and Four Dimensions

Shiladitya Sengupta,[1] Smarajit Karmakar,[2] Chandan Dasgupta,[3] and Srikanth Sastry[1,4]
[1]Theoretical Sciences Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur Campus, Bangalore 560 064, India
[2]Departimento di Fisica, Universita di Roma“ La Sapienza “, Piazzale Aldo Moro 2, 00185 Roma, Italy
[3]Centre for Condensed Matter Theory, Department of Physics, Indian Institute of Science, Bangalore 560012, India
[4]TIFR Centre for Interdisciplinary Sciences, 21 Brundavan Colony, Narsingi, Hyderabad 500075, India
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The Adam-Gibbs relation between relaxation times and the configurational entropy has been tested extensively for glass formers using experimental data and computer simulation results. Although the form of the relation contains no dependence on the spatial dimensionality in the original formulation, subsequent derivations of the Adam-Gibbs relation allow for such a possibility. We test the Adam-Gibbs relation in two, three, and four spatial dimensions using computer simulations of model glass formers. We find that the relation is valid in three and four dimensions. But in two dimensions, the relation does not hold, and interestingly, no single alternate relation describes the results for the different model systems we study.

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A central theme in the study of glass forming liquids is a satisfactory understanding of the behavior of relaxation times as the glass transition is approached, showing temperature dependence typically stronger than the Arrhenius law: $\tau(T) = \tau(\infty)\exp[\frac{E_0}{k_B T}]$ observed at high temperatures [1–3]. The Adam-Gibbs (AG) relation [4], which is of central importance in glass forming liquids, explains the behavior of the relaxation time, i.e., dynamics in terms of the configurational entropy, i.e., thermodynamics. It also forms the basis of more sophisticated theories of glass transition connecting dynamics to thermodynamics, e.g., the random first order transition theory (RFOT) [5–9]. In these theories the spatial dimensionality (D) appears explicitly in the relationship between dynamics and thermodynamics. However, the large number of experimental and numerical studies wherein the AG relation has been tested [10–17] have all been in three dimensions. The present study aims to critically examine whether the AG relation is valid in different spatial dimensions or gets generalized in a D-dependent way.

The AG relation is based on the picture that relaxation in glass forming liquids occurs through the collective rearrangement of “cooperatively rearranging regions” (CRR). The CRRs define a minimum size of groups of rearranging particles (atoms, molecules, etc., depending on the nature of the glass former) such that smaller groups of particles are incapable of rearrangement independently of their surroundings. Adam and Gibbs argued that the configurational entropy (the entropy associated with the multiplicity of distinct arrangements of particles, obtained by subtracting a “vibrational” component from the total entropy) per particle $S_c(T)$ of a liquid varies inversely as the size of the CRR, $z(T)$, since the configurational entropy per CRR, S^*, is roughly independent of temperature: $S_c(T) = \frac{S^*}{z(T)}$. The further assumption that the free energy barrier for a rearrangement is proportional to the size of the CRR ($\Delta G = z\delta\mu$, where $\delta\mu$ is the chemical potential barrier per particle) results in the AG relation:

$$\tau(T) = \tau(\infty)\exp\left[\frac{S^* k_B^{-1}\delta\mu}{TS_c(T)}\right] = \tau(\infty)\exp\left(\frac{C}{TS_c}\right). \qquad (1)$$

The above relation is obtained independent of reference to the spatial dimensionality of the system and is hence expected to be same in all spatial dimensions.

A rationalization of the AG relation, based on more detailed considerations of possible activated relaxation mechanisms, is offered by the RFOT, which has recently been discussed by many authors specifically in the context of growing length scales associated with the glass transition [18–24].

In the “mosaic” picture [5,7], the liquid is divided into metastable regions of characteristic size $\xi(T)$. The transition from one metastable state to others is hindered by the cost of surface free energy ($\Delta G_s \propto Y\xi^\theta$, where $\theta \le D$, where D is the spatial dimension and Y is the surface tension) and driven by the possibility of sampling an exponentially large number of other metastable minima (free energy gain $\Delta G_b \propto TS_c\xi^D$). There is a characteristic crossover length $\xi^*(T) \propto (\frac{Y}{TS_c})^{1/(D-\theta)}$ above which a liquid samples all metastable states and below which the liquid is trapped in one of the metastable states. The characteristic length $\xi(T)^*$ diverges as $S_C(T) \to 0$. Assuming, in general, that the free energy barrier to relaxation varies (following the notation of Ref. [9]) as $\Delta G(T) \propto \xi(T)^\psi$, one obtains

$$\tau(T) = \tau(\infty)\exp\left[\frac{A}{(TS_c)^{\psi/(D-\theta)}}\right], \qquad (2)$$

where A has weak T dependence, and $\psi = \theta$ if $\Delta G(T)$ is calculated as the free energy barrier obtained from the surface and bulk contributions above ($\Delta G = \Delta G_b + \Delta G_s$).

The mosaic picture thus contains an explicit dependence on the spatial dimension, and one recovers the AG relation only when $\frac{\psi}{D-\theta} = 1$. The original AG formulation is equivalent to assuming $\psi = D$, $\theta = 0$, whereas it was argued in Ref. [5] that $\theta = \psi = D/2$, with the AG relation as the result in both cases. In the latter case [5], a dimension independent AG relation is predicted in spite of arguments that treat spatial dimensions explicitly.

However, attempts to estimate the exponents either numerically or from experimental data are not conclusive. By direct simulation in a model liquid ($D = 3$), Cammarota *et al.* [22] obtained $\theta = 2$, $\psi = 1$ which, although consistent with the AG relation, differs from both the AG and RFOT values. The simulation study by Karmakar *et al.* [23,24] obtained $\theta \sim 2.3$ and hence $\psi \sim 0.7$ using the condition $\frac{\psi}{D-\theta} = 1$. An extensive study by Capaccioli *et al.* [20] of experimental data for 45 glass-forming liquids shows a lot of variation in both θ and ψ, with best fit estimates in the range of $\theta \sim 2$–2.15, and $\psi \sim 0.85$–1. These two studies are consistent in suggesting values of $\theta > 2$, $\psi < 1$, but both use measures of dynamical heterogeneity to extract a length scale. Since *a priori* one must expect the mosaic length to be distinct from the heterogeneity length scale, the implications of these estimates are not clear.

In view of the considerations above, the possibility of an explicit dependence of the AG relation on the spatial dimension (and within the RFOT framework, the values of the exponents θ and ψ) merits investigation. In this Letter, we address the question of the dependence on spatial dimension of the AG relation by studying model liquids in two, three, and four dimensions and evaluating the relationship between relaxation times and the configurational entropy. The evaluation of the RFOT exponents θ and ψ, while relevant to our investigation, requires the calculation of the mosaic length scale. Ways of obtaining length scales relevant to glassy dynamics that have been discussed in the literature (see, e.g., Refs. [21,23,25,26]) tend to be computationally very demanding [27]. We have therefore not attempted to evaluate the RFOT exponents in this work.

One of the well-known systems in which the AG relation is shown to be valid [15,23,28] is Kob-Andersen model (KA) [29], which is an 80:20 binary mixture of particles interacting with a Lennard-Jones potential, with Lennard-Jones parameters $\epsilon_{AB}/\epsilon_{AA} = 1.5$, $\epsilon_{BB}/\epsilon_{AA} = 0.5$, $\sigma_{AB}/\sigma_{AA} = 0.80$, $\sigma_{BB}/\sigma_{AA} = 0.88$. We truncate the interaction potential at $2.5\sigma_{\alpha\beta}$ (details as in Ref. [15]). Units of length, energy, and time scales are σ_{AA}, ϵ_{AA} and $\sqrt{\frac{\sigma_{AA}^2 m_{AA}}{\epsilon_{AA}}}$, respectively. We have studied the KA model in two (2D), three (3D), and four (4D) spatial dimensions. In addition, in two dimensions we have studied the following liquids: (1) KA model at 65:35 composition [30] which is denoted as the modified KA (MKA) model and (2) 50:50 binary mixture of repulsive soft spheres [R10 model, $V(r) \sim r^{-10}$] (see Ref. [31] for details of the model. Like the KA models, we use reduced units defined in terms of the energy scale of the model and the size of the large particles). We have performed molecular dynamics simulations in the canonical (NVT) ensemble, using the constant temperature algorithm of Brown and Clarke [32]. Simulations were done at a fixed number density ρ ($\rho = 1.2$ for the KA model in two and three dimensions, $\rho = 1.6$ in four dimensions, $\rho = 1.2$ for the MKA model, and $\rho = 0.85$ for the R10 model). Integration time steps were in the range $\in [0.001, 0.006]$ depending on T. Run lengths at each T were in excess of $100\tau_\alpha$ (the relaxation time τ_α is defined below) (e.g., at the lowest T in 4D, the total run length is $\sim 6 \times 10^8$ MD steps). The range of relaxation times accessed is up to $O(10^4)$ in three and four dimensions and up to $O(10^5)$ in two dimensions. Typically, three (1–3 in 4D, 3–5 in 3D and 2D) independent runs are performed at each T. In order to assess the influence of system size, we show results for different system sizes in two and three dimensions (indicated in appropriate places) although we do not discuss system size effects in detail here.

As a measure of dynamics, we have studied a two-point time correlation function, the overlap function $q(t)$ and its fluctuation related to dynamic susceptibility [$\chi_4(t)$] [23,33–35],

$$
\begin{aligned}
<q(t)> &= < \int d\vec{r} \rho(\vec{r}, t_0)\rho(\vec{r}, t + t_0)> \\
&\sim < \sum_{i=1}^{N} w(|\vec{r}_i(t_0) - \vec{r}_i(t_0 + t)|)> \\
\chi_4(t) &= \frac{1}{N}[\langle q(t)^2\rangle - \langle q(t)\rangle^2],
\end{aligned}
\tag{3}
$$

where $\rho(\vec{r}, t_0)$ is the space- and time-dependent particle density, $w(r)$ is the window function, $w(r) = 1$, $r \leq a$ and zero otherwise ($a = 0.3$ in 3D), and averages are obtained over initial times t_0 as well as independent samples. Relaxation times are estimated both from the condition $\langle q(\tau)\rangle/N = 1/e$ (τ_α) and the characteristic time where $\chi_4(t)$ is maximum (τ_4). As we find these two times to be proportional to each other [23], we report only τ_α.

The configurational entropy (S_c) per particle, the measure of the number of distinct local energy minima, is calculated [36] by subtracting from the total entropy of the system the "vibrational" component,

$$S_c(T) = S_{\text{total}}(T) - S_{\text{vib}}(T). \tag{4}$$

The total entropy of the liquid is obtained via thermodynamic integration [36]. The vibrational entropy is calculated by making a harmonic approximation to the potential energy about local energy minima (termed "inherent structures") [36–39].

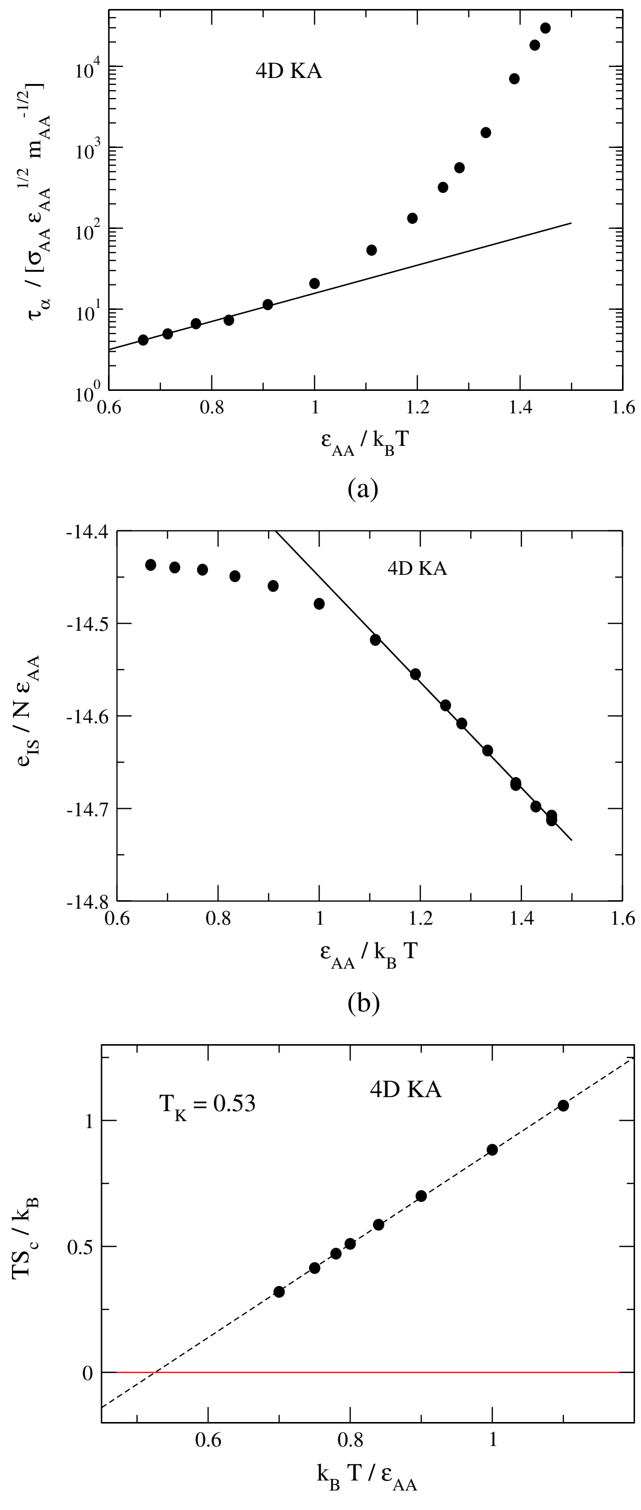
We evaluate the configurational entropy below the onset temperature (T_{onset}) across which a crossover from

Arrhenius to non-Arrhenius behavior of the relaxation time occurs [15,40,41]. In Fig. 1(a) we show this crossover in the 4D KA model. Figure 1(b) shows the temperature variation of the inherent structure energy which exhibits a $1/T$ temperature dependence below T_{onset} [15]. In Fig. 1(c), we show the T dependence of the configurational entropy for the 4D KA model. As T is lowered TS_c goes to zero linearly with T. We estimate the Kauzmann temperature (T_K) at which the extrapolated configurational entropy vanishes to be $T_K = 0.53$.

In Fig. 2, we show the AG plot for the KA model in different spatial dimensions. We see that in 4D, the AG relation is valid over several orders of magnitude of change in τ_α. As reported in earlier works, the AG relation is also valid in 3D, and the data presented in Fig. 2(b) indicates a mild system size dependence in the slopes C [Eq. (1)]. However, in two dimensions [Fig. 2(c)], we see deviations from the AG relation for low temperatures and small system sizes. It has been reported recently that the 2D KA model is prone to orientational ordering [30], which we confirm (data not shown). It is therefore not clear to what extent these observed deviations are significant. In order to ascertain the dependence of τ_α on S_c without the presence of orientational ordering, we study two other previously studied 2D models which do not exhibit significant ordering, namely the KA model with composition 65:35 (MKA) [30] and the 50:50 binary mixture of repulsive soft spheres [R10 model, $V(r) \sim r^{-10}$] [31]. Figures 3(a) and 3(b) show that for these systems, τ_α does not obey the AG relation.

We note that the nature of deviation is different in these two cases. Fitting τ_α to the generalized AG form $\tau = \tau_0 \exp[(\frac{C}{TS_c})^\alpha]$, we find $\alpha = 0.43$ for $N = 500$, $\alpha = 0.60$ for $N = 2000$ and $\alpha = 0.67$ for $N = 10000$ (i.e., $\alpha < 1$) for the MKA model, whereas for the R10 model we find $\alpha = 2.1$ (i.e., $\alpha > 1$).

The MKA model has both attractive and repulsive interactions, whereas the R10 model has purely repulsive interactions. It has recently been suggested [25] that the exponent ψ in the relation $\tau(T) = \tau(\infty) \exp[\frac{A\xi^\psi}{k_B T}]$ [see discussion preceding Eq. (2)] depends on the nature of the interactions. This possibility suggests an explanation for the results we observe which is under investigation. However, we note that in three dimensions, the AG relation has been verified in both attractive models (e.g., Kob-Andersen [15], Lewis-Wahnström orthoterphenyl [16], and Dzugutov liquid [42]) and repulsive models (e.g., repulsive soft spheres [43]). We also note that the exponent α above gets larger for larger system sizes for the MKA model. Although $N = 10000$ is a sufficiently large system as far as any relevant length scale in this model is concerned, finite-size effects as the origin of the deviation from the AG relation in these systems cannot be completely ruled out at present. Finally, we note that the behavior described here remains qualitatively the same if



(a)

(b)

(c)

FIG. 1 (color online). (a) Temperature dependence of the relaxation time τ_α of the 4D KA model displaying a crossover from Arrhenius to non-Arrhenius behavior at $T_{\mathrm{onset}} \sim 1$. The solid line is an Arrhenius fit above T_{onset}. (b) shows the average inherent structure energy vs T displaying a $1/T$ dependence below T_{onset}. (c) Kauzmann temperature for the 4D KA model, $T_K = 0.53$, is obtained from the condition $T_K S_c(T_K) = 0$.

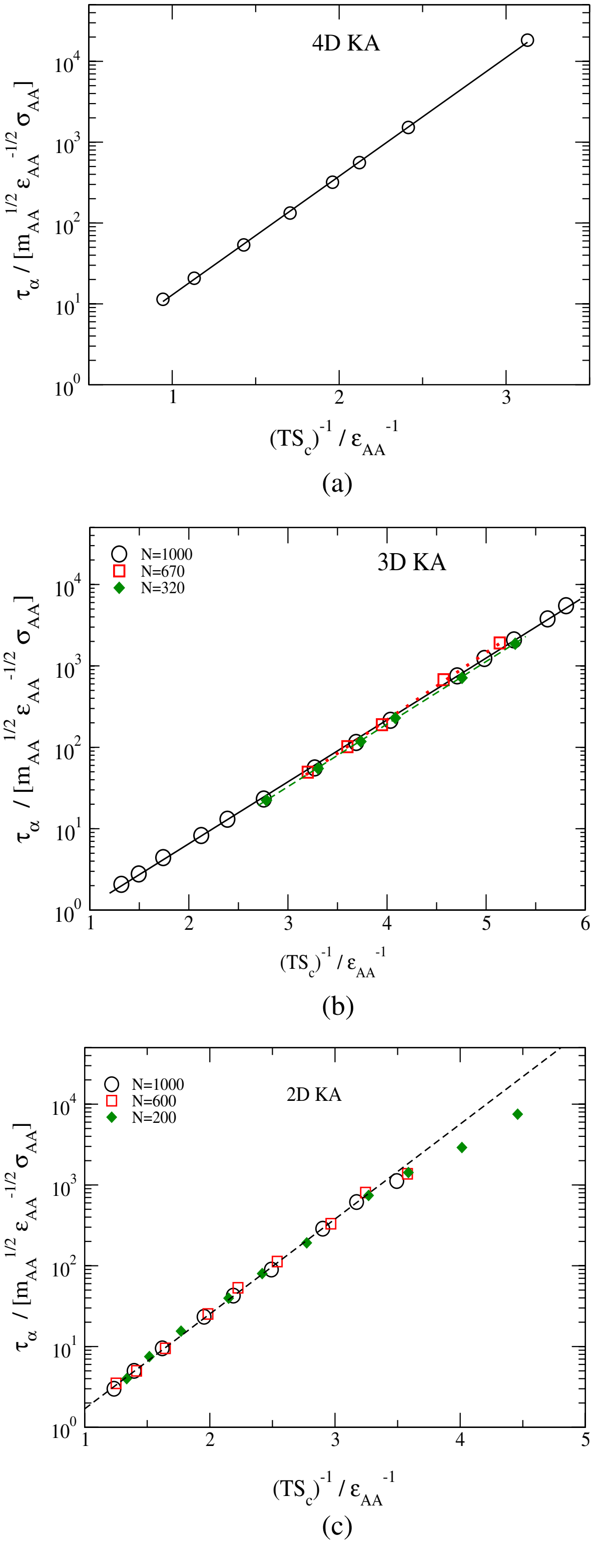


FIG. 2 (color online). Adam-Gibbs plots [τ_α vs $(TS_c)^{-1}$] for the KA model in four, three, and two dimensions. The AG relation holds in three and four dimensions but deviations are observed in two dimensions at low T and small system sizes. The system size in 4D is $N = 1500$. Lines are fits to the AG relation [Eq. (1)] (for the largest system size in the case of 2D).

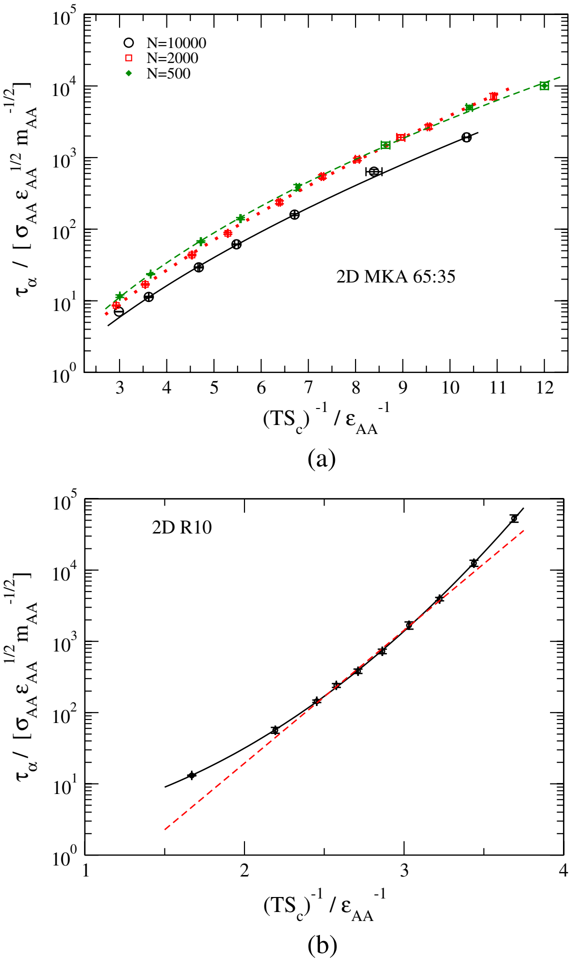


FIG. 3 (color online). Adam-Gibbs plot for the MKA and R10 models. Systematic deviations from the AG relation are seen for both models but with opposite deviations from linearity. For the MKA model, the lines are fits to the generalized AG relation of the form $\tau_\alpha = \tau_0 \exp[(\frac{C}{TS_c})^\alpha]$ [see also Eq. (2)] [$\alpha = 0.43$ for $N = 500$ (dashed), $\alpha = 0.60$ for $N = 2000$ (dotted line), and $\alpha = 0.67$ for $N = 10000$ (solid line)]. For the R10 model, the dashed line is a fit to the AG relation and the solid line is a fit to the generalized AG relation with $\alpha = 2.1$. The system size is $N = 2048$ for the R10 model.

we use inverse diffusivities instead of α-relaxation times. Such a comparison will be presented elsewhere [44] in the context of the breakdown of the Stokes-Einstein relation [45].

In summary, we examine the validity of the AG relation in different spatial dimensions by studying model liquids via computer simulations, for the first time in two and four dimensions. The AG relation is valid in four and three dimensions but is not obeyed in two dimensions, and the nature of the deviation from the AG relation depends on the details of the interaction between particles. This is an unexpected result. Although an understanding of this observation is lacking at present, they present constraints that a successful theoretical explanation of slow relaxation must meet. Such a lack of universality is unexpected and surprising since both AG and RFOT theories describe the glass transition as a thermodynamic phase transition.

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